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Progress in the Fabrication of Si_3N_4 Turbine Rotors by Pressure Slip Casting

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Abstract

The fabrication of silicon nitride components by pressure slip casting has been studied. Simple as well as more complicated shapes such as spin test discs, with homogeneous microstructure, were produced using this technique.

Prior to casting in a full-scale pressure casting machine, fundamental studies of the casting behaviour of the slips were conducted using filter pressing experiments. Due to the coarse pore structure of the polymeric mould material used, special attention was given to the slip properties in order to avoid slip penetration into the mould and to obtain an adequate consolidation. Parameters like the degree of particle interaction and solid content as well as the pressure schedule were investigated.

Partially flocculated slips were found to give considerably faster castings and the obtained bodies sintered to nearly full density without deformations In pressure casting of spin test discs with stabilized slips, optimization of the pressure schedule was required to avoid cracking caused by stress gradients.

Die Herstellung von Siliziumnitridkomponenten mittels Preßschlickergießens wurde untersucht; sowohl einfache als auch kompliziertere Formen, wie z.B. Rotationsteststcheiben wurden mit einem homogenen Mikrogefüge hergestellt.

Vor dem Gießen in einer Druckgießmaschine wurde das Gießverhalten des Schlickers mit Hilfe von Filterpreßexperimenten untersucht. Infolge der großporigen Struktur der Polymergießformen wurde besonders auf die Schlickereigenschaften geachtet, um ein Eindringen des Schlickers in die Form zu vermeiden, und um eine ausreichende Verdichtung zu erreichen. Dabei wurden Parameter wie die Wechselwirkung der Teilchen, der Feststoffgehalt und der Preßdruckverlauf betrachtet.

Mit teilweise ausgeflocktem Schlicker konnte eine deutlich höhere Gießgeschwindigkeit erreicht werden, und die Korper konnten, ohne sich zu verformen, zu nahezu voller Dichte gesintert werden. Beim Druckgießen von Rotationsteststcheiben mit stabilisiertem Schlicker war eine Optimierung des zeitlichen Druckverlaufs notwendig, um Rißbildung zu vermeiden.

Le travail présenté concerne l'étude de la fabrication par coulage sous pression, de composants en nitrure de silicium. Des formes aussi bien simples que compliquées et présentant une microstructure homogène ont été produites par cette technique.

Avant l'étape de coulage sous (pression, une étude fondamentale du comportement au coulage des barbotines a été réalisée par des expériences sur filtres-presses. Etant donné la porosité grossière des moules en polymère utilisés, une attention spéciale a été portée sur les propriétés de coulage, afin d'éviter la pénétration de la barbotine dans le moule et d'obtenir une consolidation adéquate. L'effet de paramètres tels que les interactions entre les particules, la teneur en matière sèche et la pression ont été étudiés.

Des barbotines partiellement floculées permettent un coulage très rapide et conduisent à des matériaux complètement densifiés sans déformations. Le coulage sous pression des formes compliquées avec des barbotines stabilisées, demande l'optimisation de la pression, afin d'éviter la fissuration due à des gradients de contraintes.

1 Introduction

Today there exist two major forming techniques for large-scale fabrication of ceramic components with complex shapes: injection moulding and slip casting. In injection moulding relatively large amounts of polymers (40–50 vol.%) are added,

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which have to be removed before sintering. This burnout stage of polymeric binder is very time-consuming if the component has thicker parts and cracks are to be avoided. In the slip casting process there is a liquid (mainly water) which has to be removed from the cast component. This drying stage is much easier to perform than the binder burnout process. Furthermore, as a liquid-based forming technique the slip casting process has the potential of giving more homogeneous, dense particle packing and hence a more favourable microstructure.

During the past 15 years the original slip casting process has developed into a more advanced process, pressure slip casting. Unlike slip casting, in which the filtration originates from capillary action (0·1–0·2 MPa) in plaster of Paris moulds, pressure slip casting derives its driving force from an external pressure (<4 MPa) applied to the ceramic suspension. The porous moulds used in pressure slip casting consist of polymeric materials with much larger pores than conventional moulds of plaster of Paris. Moulds of polymeric materials and application of high pressure give a number of advantages as opposed to conventional slip casting: (i) much faster casting which minimizes settling and/or segregation effects; (ii) better mould durability and hence improved reliability; (iii) less space requirement because drying of the moulds is not necessary. The polymeric moulds can be used for at least 10000 cycles, which is about 100 times more than for the plaster moulds.

Pressure slip casting is nowadays an established forming technique in fabrication of traditional clay-based ceramic materials such as pottery and sanitary porcelain.[1] However, commercial production of technical ceramics by pressure slip casting is still very limited. In pressure slip casting of traditional clay-based materials, the powder particles are relatively coarse with a wide particle size distribution. Furthermore, the slips are usually not fully stabilized, i.e. they are partially flocculated, which promotes the consolidation and favours the plasticity of the green compact.[2] In the production of high-performance ceramics very fine powders are used (<1–2 μm) and the slips are most often highly stabilized, i.e. the particles are effectively kept apart by repulsive forces. The use of submicron powders and highly stabilized slips gives a significant risk of slip penetrating the porous mould surface, and consequently no adequate consolidation occurs. This problem is obvious when considering that the pore size in the polymeric mould material is in the range of 30–40 times larger than the particles.

To be able to use pressure slip casting for casting of submicron non-clay materials, such as silicon nitride, the properties of the slip have to be optimized in terms of solid loading, particle size distribution and degree of stabilization. So far, very few systematic studies of this subject have been done and published.

There are some factors which are especially critical in large scale pressure slip casting. First of all, since a large amount of slip is prepared, which will be used for several days, it is important that the rheological properties of the slip are constant over time. Settling or flocculation will lead to pure process problems, such as clogging of slip tubes and valves. In addition, there will be difficulties in obtaining constant green properties and consequently reproducible properties of the final components.

The design of the mould is very critical in order to achieve components which are easy to demould without critical stresses. If the mould consists of two porous polymeric mould halves, two consolidated layers are formed which will approach each other in the centre of the compact. Casting in two directions will give a very fast casting process, but there is always a risk that a defect will be obtained at the centre of the compact, where the two cast fronts meet. Alternatively only one porous mould is used and a unidirectional casting is obtained, where only one cast layer is built up and hence, centre defects are avoided. It can be mentioned that it is very common to use two porous mould halves in the fabrication of porcelain by pressure slip casting. However, in that case, such defects (as possible centre defects) are usually not as critical as they would be in the fabrication of high performance ceramics.

In this paper, the pressure slip casting of Si_3N_4 has been examined. Although the final goal is to produce turbine rotors, this work can be seen as a pre-stage in which a fundamental understanding of the factors which influence the pressure slip casting process has been obtained. For this purpose simple as well as more complicated shapes, such as spin test discs (pre-stage to turbine rotor) have been produced. Prior to the castings in the pressure casting machine, studies of the casting behaviour of the slips were conducted by using filter pressing experiments. Filter pressing in a laboratory pressure filtration device has proven to be an excellent method to characterize the consolidation behaviour of ceramic slips, including the permeability and compressibility of the cake.[3-7] It has to be noted that the main aim of the filter pressing experiments was not to correlate the results to theoretical models, but to use it as a tool in order to (i) examine the consolidation behaviour of different slips, (ii) test the filter materials (and penetration), and (iii) test different pressure schedules, i.e. simulate casting processes in laboratory scale before the castings in the full-scale machine.

2 Theory

Since slip casting as well as pressure slip casting are filtration processes, it is possible to derive expressions from the filtration theory which describe the consolidation process. The expressions developed from the filtration theory take into consideration both the filtration resistance through the consolidated layer and the resistance through the mould.[3,8] The mould filtration resistance will influence the casting rate when using plaster moulds and relatively coarse powders, or not fully stabilized suspensions. On the other hand, Aksay & Schilling[8] have found that the filtration resistance in the plaster mould becomes negligible compared to the resistance in the consolidated layer in slip casting with submicron particles and highly concentrated slips (above 35 vol.%). In pressure slip casting or filter pressing, when using polymeric moulds with about 40 times larger pores than in plaster moulds, the dismissal of the filtration resistance becomes even more permissible.

Figure 1 illustrates the development of a filter cake on a porous filter in which the mould resistance has been neglected. The externally applied pressure, P, builds up a liquid pressure, P_L, during a time t, which drops when getting closer to the filter. Simultaneously, the pressure on the solid, P_s, rises in an accumulated way and reaches a maximum at the filter surface.

The shape of the pressure distribution in the consolidated layer (Fig. 1) depends on the degree of compressibility.[4,7,9] The compressibility is very pronounced for filter cakes obtained from flocculated slips. In such a case, the major pressure drop is close to the filter, and a non-linear relation of the casting rate (x^2/t) as a function of applied pressure is obtained.[6,7] On the other hand, a highly stabilized slip gives an almost incompressible filter cake and the pressure drop is nearly linear throughout the cake.

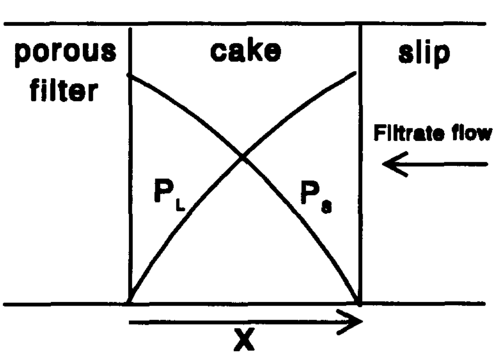

Fig. 1. Schematic illustration of the consolidation process during filter pressing. P_L and P_s represent the liquid pressure and the solid pressure, respectively.

A model for the consolidation process in filter pressing, which can be adapted to all kinds of pressure schedules, has been constructed. The model is simplified by neglecting the compressibility of the consolidated layer and the filtration resistance of the mould. It is also assumed that the slip properties are constant during the filtration process, i.e. the colloidal stability and the solid content of the slip are constant during the casting process.

A mathematical description of the consolidation process starts with Darcy's law for a flow, q, through a porous medium:

$$q_x = \frac{1}{A}\frac{dV}{dt} = \frac{k}{\eta}\frac{dP}{dx} \tag{1}$$

where A is the filtration area, dV/dt the rate of the filtrate flow, dP/dx the pressure gradient over the porous medium (the consolidated layer with the thickness x), η the viscosity of the liquid phase, and k is the permeability of the consolidated layer.

In filter pressing the cross-section area, A, is constant and consequently the liquid flow, V/A (m^3/m^2) is equal to the plunger movement, D. If it is assumed that no particles penetrate the filter, a mass balance, based on solids (see Fig. 2) will give

$$\varepsilon_0(D + x) = \varepsilon_s x \Rightarrow D = \frac{V}{A} = \left(\frac{\varepsilon_s}{\varepsilon_0} - 1\right)x \tag{2}$$

where ε_0 and ε_s are the volume fractions of solid particles in the slip and the consolidated layer, respectively.

Equation (1) then turns to

$$\left(\frac{\varepsilon_s}{\varepsilon_0} - 1\right)\frac{dx}{dt} = \frac{k}{\eta}\frac{dP}{dx} \tag{3}$$

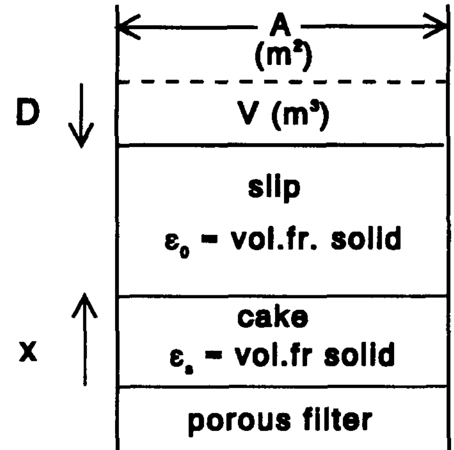

Fig. 2. Illustration of the conditions in filter pressing. The plunger movement, D, is equal to the filtrate volume per area, V/A, passed into the filter.

From eqn (3), $d^2P/dx^2 = 0$ since $(\varepsilon_s/\varepsilon_0 - 1)$ is assumed to be time independent. This means that there is a linear pressure gradient over the consolidated layer and dP/dx can be replaced according to:

$$\frac{dP}{dx} = \frac{P(t)}{x(t)} \quad (4)$$

and finally eqn (3) can be written as

$$x(t)\frac{dx}{dt} = \frac{k}{\eta\left(\frac{\varepsilon_s}{\varepsilon_0} - 1\right)} P(t) \quad (5)$$

Integrating eqn (5) over a time interval $t_i - t_{i-1}$, the cake thickness change, which has consolidated during this interval, can be expressed in the following form:

$$x^2(t_i) - x^2(t_{i-1}) = 2\frac{k}{\eta\left(\frac{\varepsilon_s}{\varepsilon_0} - 1\right)} \int_{t_{i-1}}^{t_i} P(t)\, dt \quad (6)$$

Since P either increases linearly or is constant, $P(t)$ is a simple function and hence, based on eqn (6), the consolidation process can be described in a simple way. Different relations for the permeability can then be extracted depending on the pressure cycle used. Note that the cake growth in each pressure sequence is dependent on the previous history of the pressure cycle. Figure 3 gives two examples of pressure cycles used in this study and the corresponding expressions for the permeabilities are derived from eqn (6) and give for the pressure cycle in Fig. 3(a)

$$k = \frac{x^2(t_2)\eta\left(\frac{\varepsilon_s}{\varepsilon_0} - 1\right)}{P_1(2t_2 - t_1)} \quad (7)$$

and for the pressure cycle in Fig. 3(b)

$$k = \frac{x^2(t_3)\eta\left(\frac{\varepsilon_s}{\varepsilon_0} - 1\right)}{P_1 t_2 + P_2(2t_3 - t_2 - t_1)} \quad (8)$$

These expressions give an average permeability for the whole filtration process. Thus, in a comparative study, this model makes it possible to characterize the casting properties of different slips. It has to be pointed out that eqn (6) will be less reliable when the filter pressing is conducted with a flocculated slip.[4,7] Consolidation of flocs may result in significant compressibility of the cake, and hence non-constant permeability during the casting process.

Flocculation increases the casting rate due to a decrease in density and the time saving will therefore be significant when casting thicker components. However, it is essential to provide an adequate control of the flocculation and the resulting consolidation behaviour in order to avoid density gradients.

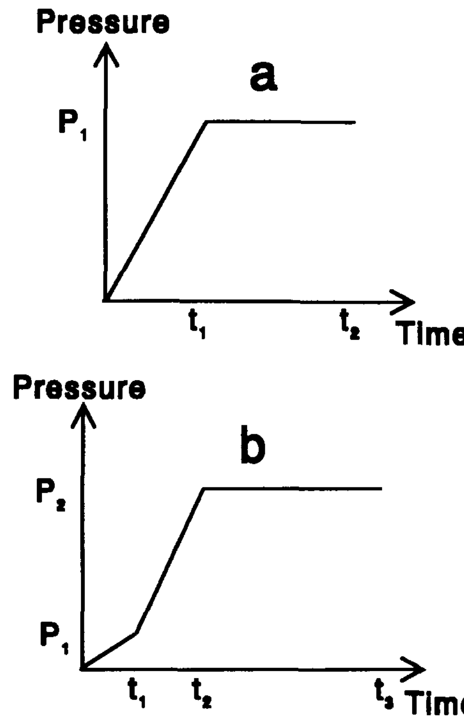

Fig. 3(a) and (b). Examples of pressure schedules for filter pressing used in this study.

3 Materials and Methods

3.1 Powder and slip preparation

The Si_3N_4 powder mainly used in this study was P95 from KemaNord Industrikemi/Permascand, Sweden, with a BET specific surface area of 7·0 m^2/g (Flowsorb II 2300, Micromeritics). However, experiments were initially also performed with a finer Si_3N_4 powder (UBE-E10, Japan) with a BET specific surface area of 10·2 m^2/g. As sintering additive an Y_2O_3 powder (fine grade, HC Starck, Germany) with a BET specific surface area of 9·2 m^2/g was used. The water-based slips (96 wt% Si_3N_4, 4 wt% Y_2O_3), with a solid content of 70–73·2 wt% (42–44·9 vol.%) were prepared by additions of anionic polyelectrolytes as dispersants, 0·10 wt% polyacrylic acid (=PAA; Dispex A40, Allied Colloids, UK) at pH 9–9·4 or 0·20 wt% lignosulphonate (=LS, Wargonin Extra, Holmen Lignotech, Sweden) at pH 9·8–10·2. The slips were homogenized by ball milling (Si_3N_4 balls) for 70 h. The particle size distribution of the powder mixture was measured by X-ray sedimentation (Micromeritics 5000 ET) after the milling. Before the slips were used for casting, they were conditioned for more than 2 days until all gassing was finished. In order to remove hard agglomerates or contaminants from the ball-milling the slips were

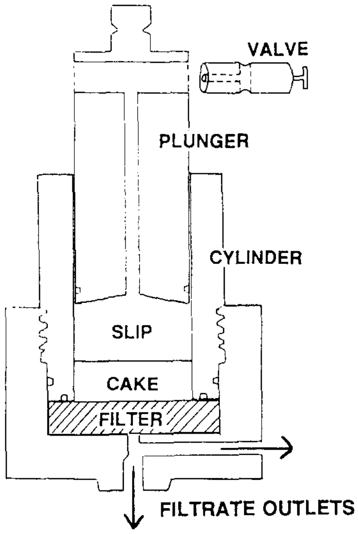

Fig. 4. Filter press constructed for use in a universal testing machine.

sieved through a cloth with suitable pore size (50–90 μm) prior to the casting. In some experiments, a partial flocculation was introduced by additions of small amounts of polyethyleneimine (= PEI; Catiofast PL, BASF, Germany) to the originally stabilized slips.

Prior to further experiments, viscosity measurements were performed using a rotary viscosimeter (Rheomat 30, Contraves). The apparent viscosities, at low to high shear rates, of stabilized as well as flocculated slips, were measured. Evaluation of the long-term rheological behaviour was performed by viscosity measurements after certain times of stirring. As a complementary check of the slip stability, small discs were slip cast.

3.2 Filter pressing

The filter press (Fig. 4) was constructed for adaptation in a universal testing machine (Zwick 1464) which permits control of the pressure (load) as well as the plunger movement. The polymeric filter material used was of a commercial type (Gebrüder Netzsch, Germany), delivered in two versions, one with a coarser (20–50 μm) and one with a finer pore structure (15–30 μm). The pore size distributions of the filter materials were measured by Hg intrusion (Micromeritics Pore Sizer 9305), see Fig. 5. The mould material, HF 63, with larger pores is the conventional mould material used for casting traditional clay-based materials. The filter with the finer pore size (63F) was developed for casting of technical ceramics and this type of filter was used in most of the experiments. In order to simulate realistic conditions, no sieve or filter paper was placed on top of the filter material. In the filter experiments with stabilized slips, various solid loadings and various pressure schedules were tested. By collecting the filtrate, it was possible to measure the amount

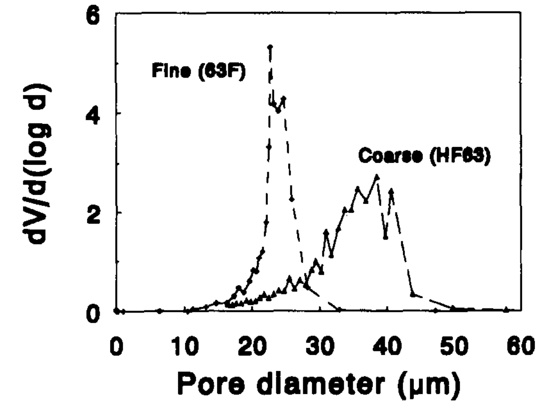

Fig. 5. Pore size distributions of the two types of polymeric filter materials (63F and HF63, Gebrüder Netzsch, Germany), measured by Hg intrusion.

of solid material which had penetrated the filter. Filter pressing was also conducted at various degrees of flocculation. Green densities were measured and permeabilities were calculated. Selected filter pressed bodies were sintered using hot isostatic pressing (1775°C, 160 MPa, 1 h) at AC Cerama AB, Sweden.

3.3 Pressure casting

After evaluation of the initial results, casting experiments with the P95 powder were performed in a pressure casting machine (Netzsch, type 225.01Ex, Germany) with stabilized (0·1 wt% PAA or 0·2 wt% LS) as well as with partially flocculated slips (0·1 wt% PAA + 0·04 wt% PEI). This pressure casting machine is a small production unit with the ability to cast at a maximum pressure of 4·0 MPa. The largest article to be cast is 1200 cm^3 at 3·0 MPa. The machine is equipped with a separate pressure–time-control unit enabling pressure schedules to be programmed in up to 100 sequences.

Initially, plates were cast using two porous mould halves. Then unidirectional casting of discs, cones and spin test discs was performed using one porous mould half and one solid mould half made of PVC. All porous moulds used in the pressure casting experiments were made of the fine-pore-sized material. The know-how in manufacture of porous moulds had been transferred from Netzsch.

In the pressure casting of the spin test discs with relatively complicated shapes, the work included design and fabrication of the mould. Pressure cast components were HIPed at AC Cerama AB.

4 Results

4.1 Powder and slip properties

It turned out that the P95 powder had properties which were highly suitable for pressure casting. It was easy to disperse, and much higher solid load-

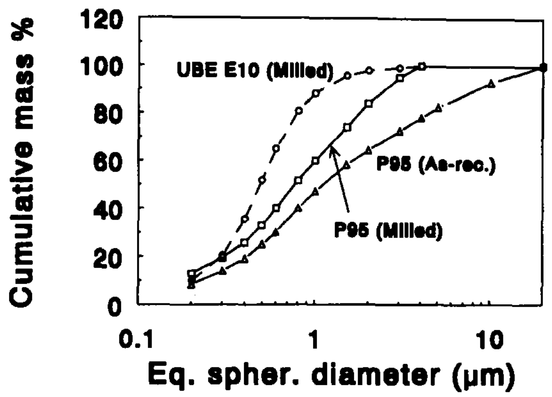

Fig. 6. Particle size distribution of the Si_3N_4 powder (P95) from KemaNord/Permascand; as-received and after ball milling (with 4 wt% Y_2O_3). The particle size distribution of the milled UBE powder (E 10) is shown as a comparison.

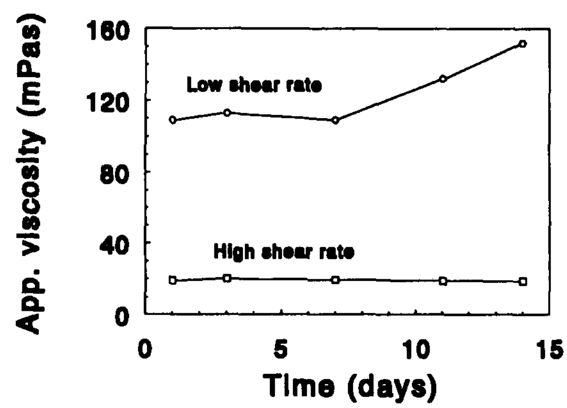

Fig. 8. Long-term study of the apparent viscosity of a Si_3N_4 slip (P95 with 4 wt% Y_2O_3) stabilized by lignosulphonate.

ings and green densities were obtained compared to what was reached with the finer E10 powder. This is probably explained by the relatively wide particle size distribution (Fig. 6) of the P95 powder which permits very good particle packing. As a consequence, most of the published results concern the P95 powder from KemaNord/Permascand.

Pre-studies showed that Si_3N_4 slips with the highest stability, i.e. the lowest viscosity, were achieved by either addition of 0.1 wt% of the polyacrylic acid at pH 9 or addition of 0·2 wt% of the lignosulphonate at pH 10. The optimal amounts of either the PAA or the LS gave similar pseudoplastic, low-viscosity slips (Fig. 7). The pseudoplastic behaviour, i.e. reduced viscosity at increased shear rate, is very typical for slips with high solid loadings of stabilized particles. The slips also showed constant long-term rheological properties. As an example, the results from the long-term study of the Si_3N_4 slip stabilized with lignosulphonate are seen in Fig. 8. After 11 days of stirring, just a slight increase in the viscosity at the lowest shear rates was observed.

In slip casting, green densities as high as 63–66% of theoretical density (TD) could be obtained with the P95 powder. In comparison, it can be mentioned that the UBE powder only reached green densities in the range of 57–59 % of TD.

If too much powder was used at the ball-milling, the slips with polyacrylic acid were partially destabilized. This phenomenon was not observed when using lignosulphonate as dispersant. The lignosulphonate molecules are reported to be almost spherical with a negative charge at pH > 3, and it has been suggested that the LS molecules stabilize particle suspensions at high pH without being adsorbed at the particle surfaces.[10] On the other hand, slips stabilized with polyacrylic acid showed a more stable pH compared to slips with lignosulphonates where the pH had a tendency to decrease with time.

Figure 9 shows the effect on the viscosity and the slip cast density, when adding the cationic polyethyleneimine (PEI) to a slip stabilized with the anionic polyacrylic acid. The significant increase in the viscosity gave a clear indication that flocculation had really occurred. The function of the positive polyelectrolyte is to shield the negative

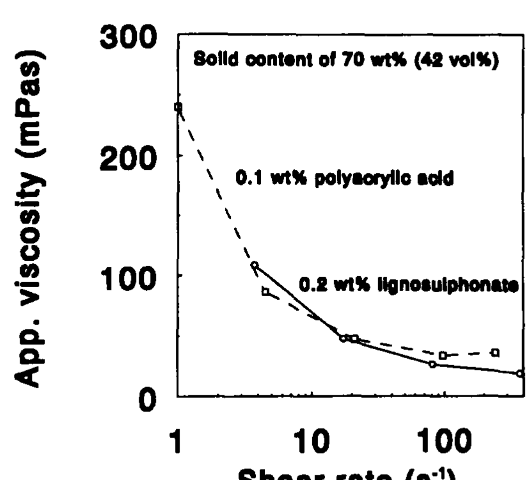

Fig. 7. The apparent viscosity versus shear rate for Si_3N_4 slips (P95 with 4 wt% Y_2O_3) stabilized with either polyacrylic acid or lignosulphonate.

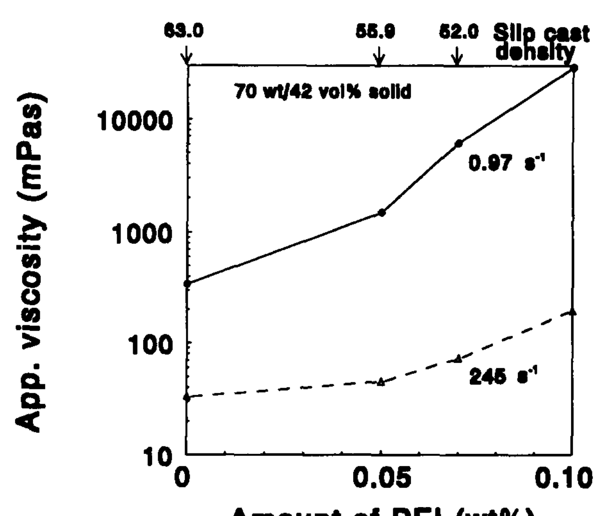

Fig. 9. The effect on the apparent viscosity and the slip cast density when adding PEI to a Si_3N_4 slip stabilized with polyacrylic acid.

charge of the polyacrylic acid and to form 'bridges' between different PAA molecules. The partial flocculation was also confirmed by the decreased green density of slip cast discs, from 63% (no PEI) to 52% (0·07 wt% PEI added) of theoretical density. Unfortunately, the partial flocculation created inhomogeneities (large structures) in the slip, and also a considerable thixotropic behaviour. However, this effect could be limited by new additions of polyacrylic acid without total deflocculation of the slip. When extra PAA was added, the large structures disappeared, the slip became homogeneous and the thixotropy was decreased significantly. High viscosity and low green density of slip cast discs indicated that flocculation still existed. This phenomenon was further utilized in the pressure casting experiments.

4.2 Filter pressing

4.2.1 Application of external pressure

In the first filter pressing experiments with the P95 powder, using the coarse filter material, various speeds of pressure increase were tested. When using a slip stabilized by lignosulphonates, with a solid content of 70 wt% (42 vol.%), consolidation occurred at a low speed (3 min up to 4·0 MPa) and at a high speed (5 s up to 4·0 MPa). However, at an intermediate speed (30–60 s up to 4·0 MPa) the slip went through the filter without consolidation. This was in agreement with the pseudoplastic properties of the slip, see Fig. 7. At a low plunger speed, corresponding to a low shear rate, the viscosity is high. Here, the particle interactions are dominating and the Brownian motion gives a disordered structure which favours the consolidation. At the intermediate plunger speed, where the hydrodynamic forces dominate and the particles are ordered in a layered structure, the slip has the lowest viscosity. Under such circumstances, the slip penetrates the filter more easily and no consolidation occurs. The consolidation at the highest plunger speed was most likely due to increased viscosity at very high shear rates, over the limit for the viscosimeter used. At such high shear rates, turbulence phenomena often appear as a dilatancy behaviour of the slip, i.e. increased viscosity at increased shear rates. This behaviour can be explained by a break up of the ordered particle structure. Consequently, the resulting disordered structure at a fast pressure increase promotes consolidation. Based on these results, a slow initial increase was chosen in most experiments to minimize the penetration of particles into the pores of the mould.

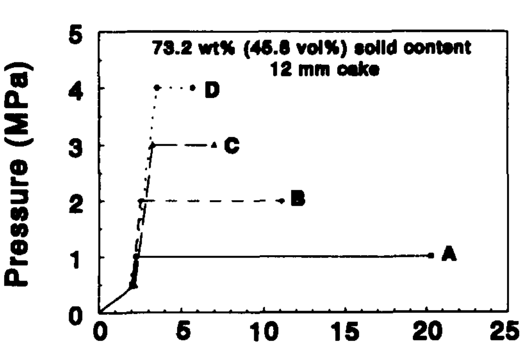

Fig. 10. Pressure schedules to obtain a 12 mm cake in filter pressing with a Si_3N_4 slip, stabilized with lignosulphonate.

Figure 10 illustrates how the casting time in filter pressing is reduced with increased pressure. A slow pressure increase gave the initial consolidation. The first consolidated layer, with its small pores, permitted a faster pressure increase without penetration problems. As Table 1 shows, the amount of solid penetrating the filter appeared to be negligible. Even when the coarser filter material was used, the amount of solid penetrating the filter remained at 1·4 wt% of the total cake weight. In this study a slip with a relatively high solid content was used, 73·2 wt% (45·8 vol.%) and, in general, it is an advantage with a high solid content which reduces the risk of penetration, and hence the rate of the pressure increase will be less critical. The four cast specimens (A, B, C and D) in Fig. 10, with a height of 12 mm, were examined by three different techniques in order to study possible segregation effects developed during casting. BET specific surface area measurements, scanning electron microscopy and Hg porosimetry were used to analyse the lower, middle and top layers of the specimens. No gradients or segregation effects could be detected. This is also what is expected when stabilized slips are used.

The permeabilities of the cast components were determined from eqn (8) (see also Fig. 3(b)) and the results are seen in Table 1. As expected the permeabilities were relatively low, which is significant when using stabilized systems. Dispersed, stabilized slips promote dense and homogeneous packing of particles which, in turn, gives a low and constant permeability throughout the consolidated layer, i.e. the compact is incompressible.

Table 1. Results from filter pressing of a stabilized P95 slip with a solid content of 45·8 vol.%

Sample	*Filter*	*Maximum pressure (MPa)*	*Penetration (wt%)*	*Green density (% TD)*	*Permeability (10^{-7} m^2)*
A	Fine	1·0	0·4	63·9	2·5
B	Fine	2·0	—	63·6	2·5
C	Fine	3·0	0.4	63·5	3·1
D	Fine	4.0	0·3	62·4	3·8
E	Coarse	4·0	1·4	62·5	4·3

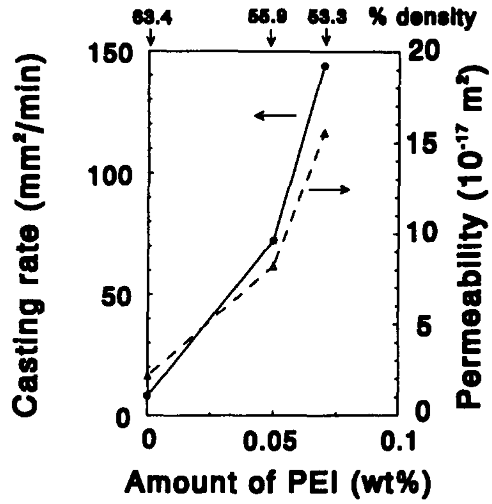

Fig. 11. The effect on the casting properties in filter pressing, when adding PEI to a stabilized Si_3N_4 slip.

However, the results showed an increase in the permeability and a corresponding decrease in the green density with increased pressure. This indicates that, to a certain extent, a higher pressure has influenced the consolidation process, giving less dense particle packing. Despite this fact, the green body investigations did not show any detectable gradients. Thus, the lower green densities could not be explained by compressibility effects.

Introducing instability of the slip by addition of the polyethyleneimine increased both the casting rate and the permeability considerably compared with the use of a stabilized slip (see Table 1 and Fig. 11). Although the green densities decreased when the slips were flocculated, from 63 to 53% of theoretical, the time-saving was significant, especially when considering casting of thick components. Of course, this requires that homogeneity exists in the body, i.e. there are no density gradients. It has to be mentioned that these permeabilities were calculated from eqn (7) in which it has been assumed that the pressure gradient over the consolidated layer is linear, i.e. the layer is incompressible. In general, a flocculated slip gives more compressible bodies than a stabilized slip, due to the more open structure after consolidation. However, 30–40 mm thick filter cakes, obtained from partially flocculated slips (0·05 and 0·07 wt% PEI added), sintered to 99·9% of theoretical density without detectable deformations. This indicates that, at least up to this degree of flocculation, it must be an almost incompressible cake and hence, eqn (6) can be used to give an approximate value of the casting rates and permeabilities.

Filter pressing with stabilized UBE-E10 powder was also conducted. However, despite the use of the finer filter material, an increased solid loading (up to 42 vol.%) and properly adjusted pressure schedules, the slip totally penetrated the filter without any consolidation. Consequently, the P95

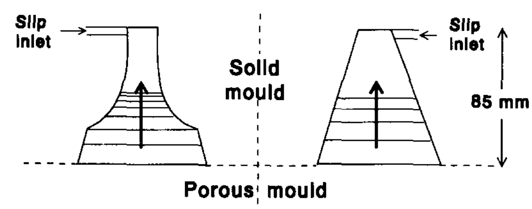

Fig. 12. Description of the two conical moulds used in the pressure slip casting experiments. The progress of the consolidated fronts are illustrated.

powder was chosen in all the following pressure castings.

4.3 Pressure casting

4.3.1 Casting with two porous mould halves versus unidirectional casting

In the first generation of pressure slip cast materials, discs (60 × 60 × 7 mm) were cast using a mould with two porous mould halves. Stabilized slips with solid contents >42 vol.% were used in these experiments. Consolidation occurred and plates were pressure cast, without any penetration problems. It was also shown that, by using an optimized pressure schedule, the growing cast fronts may come in such close contact that centre defects are minimized or even avoided.

To eliminate all risks of centre defects, unidirectional castings with one porous mould and one solid mould (made of PVC) were used in the later generations of pressure cast materials, such as plates, cones and spin test discs.

4.3.2 Pressure casting of thick components

Two cone-shaped moulds were fabricated to study the unidirectional casting of thick components, see Fig. 12. In most of the castings, stabilized slips were used. However, since the casting time in the unidirectional casting of thick (>50 mm) components, will be relatively long, experiments were also performed with partially flocculated slips.

In Table 2, some of the results from castings of the more simply shaped cone (Fig. 12, right) with the stabilized slip are seen. At all castings, except No. 5, a 30 s ramp up to the top pressure was

Table 2. Pressure slip casting of cones with a stabilized Si_3N_4 (P 95) slip

Sample	*Pressure (MPa)*	*Casting time (min)*	*Height (mm)*	*Green density (%)*
1[a]	2·0	30	33	59·1
2[a]	2·0	83	50	59·3
3[a]	3·0	83	74	59·8
4[a]	4·0	40	61	59·1
5[b]	3·0	165	51	59·2

[a] 30 s up to the pressure.
[b] No holding time at the pressure.

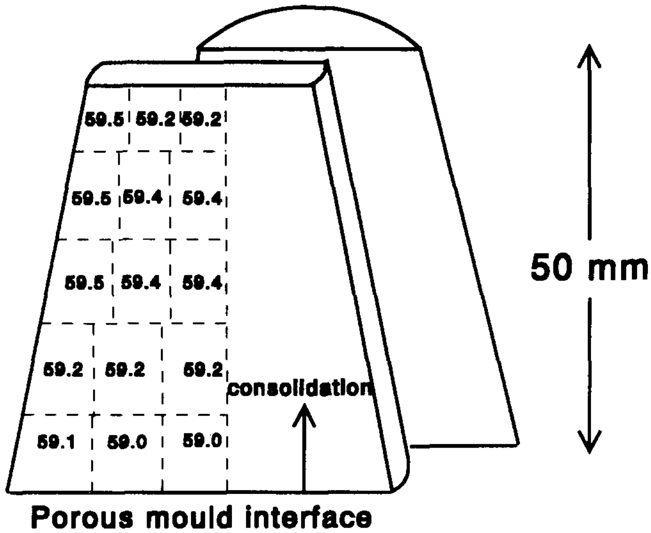

Fig. 13. Relative densities (% of theoretical) of cut pieces of the pressure cast and pre-sintered cone No 2.

used. The densities were all in the range of 59–60%. Cone 2 was more thoroughly investigated concerning density gradients. After pre-sintering at 1750°C to obtain interparticle binding without shrinkage, the cone was cut into pieces, as illustrated in Fig. 13, and the densities were measured by the water intrusion method. A slight increase in the density from the bottom to the top of the cone could be seen. This was not expected, because the theory predicts a higher density towards the mould surface due to the pressure gradient during casting. A possible explanation could be that a small fraction of fine particles penetrated the mould during the early stage of the casting process. There is also a tendency to a very slight density increase from the centre to the periphery of the cone. This increase, however, is so small that it has to be further verified by other measuring techniques. Although there was a small density difference in the cast body, no inhomogeneous shrinkage could be detected after HIPing.

The casting of the two types of cones illustrates the importance of a proper mould design. In pressure casting of the simply shaped cone, there were no difficulties in demoulding the component. In contrast, there were many more release difficulties with the cone which was more tapered (Fig. 12, left). These problems were mainly related to the expansion of the green body after the pressure release, and the fact that the mould for the more tapered cone did not have as good relief angles as the mould for the more simply shaped cone. It is also possible that the mould relaxed when the pressure was released, which then additionally compressed the green body. The difficulties with the demoulding became worse when higher pressures were applied. In practice the maximum pressure was about 2.0 MPa for casting this component.

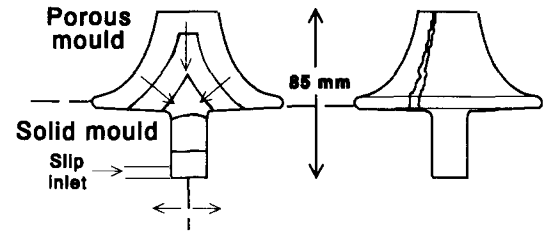

Fig. 14. Description of the spin test disc mould and illustration of the consolidation progress during casting. To the right a radial crack is illustrated.

By using a flocculated slip (0·1 wt% PAA + 0·04 wt% PEI) a cone (Fig. 12, left) with the height of 78 mm was obtained after 38 min at 2·0 MPa. This was 2–3 times faster than when using a stabilized slip. The green density of the cast compacts from the partially flocculated slip was about 55% of theoretical density, to be compared to a green density of 59–60% obtained with the stabilized slip. However, when using the partially flocculated slip, problems arose with clogging of the slip tubes, which tended to interrupt the casting process. These problems were solved by further addition of small amounts of the dispersant. The fact that a partial flocculation still existed after the addition of dispersant was confirmed by the slight increase in green density, from 55 to 56% of theoretical density.

4.3.3 Pressure casting of spin test discs

The mould for the spin test disc was designed as Fig. 14 shows. When casting with stabilized slips (using polyacrylic acid), there were initial problems with radial cracks as illustrated in Fig. 14. These cracks appeared during the release of the pressure, during the demoulding or during the initial drying. The problem with the critical stresses was probably due to stress gradients in the compact and rigid green properties. However, when a lower pressure was used, the plasticity of the cast compact increased and the tendency of crack initiation decreased. Still, careful drying was needed to avoid cracks. Some of the results from pressure casting of spin test discs are summarized in Table 3. The best results were obtained when a ramp (linear pressure increase) was used for the initial casting of the 'top' of the spin test disc, performed in the porous mould, and then a constant

Table 3. Results from the pressure slip casting of spin test discs

Sample	*Pressure schedule (min) → (MPa)*	*Total casting time (min)*	*Green density (%)*	*Cracks*
IIa	10 → 2·0	140	61	Yes
IIb	10 → 3·0	90	61	Yes
III	15 → 0·7	220	60	No

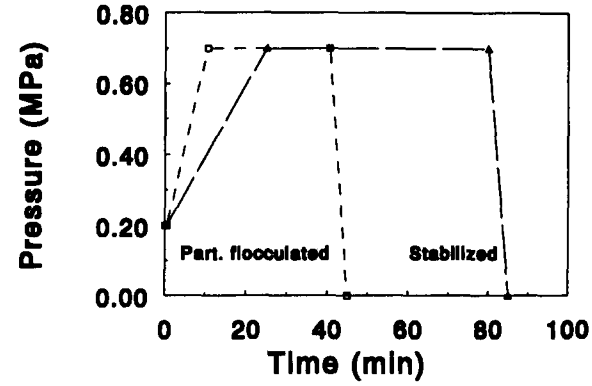

Fig. 15. Examples of pressure cycles used for pressure slip casting of spin test discs with stabilized and partially flocculated Si_3N_4 slips respectively.

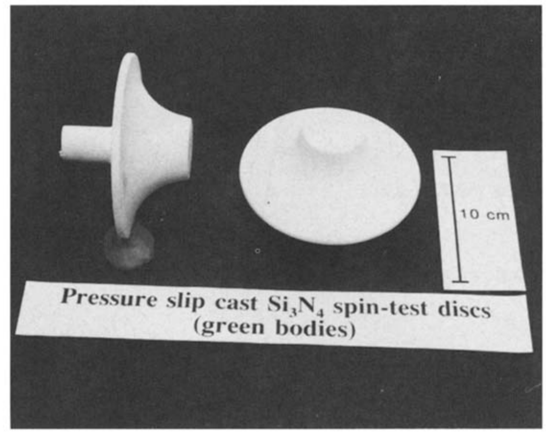

Fig. 16. Pressure slip cast spin test discs (green compacts).

pressure (less than 0·7 MPa) was used for casting of the thin shaft in the solid mould. The need of a relatively low maximum pressure to avoid critical stress gradients and hence also crack initiation, gave considerably longer casting times; 1·5–4·5 h, depending on the slip properties (solid loading, rheology, particle size distribution, etc.). The time for casting the wider 'top' part of the spin test disc is short, 15–25 min, because it is performed in a porous mould part and the filtration area is large. Most of the total casting time (more than 1·5 h) is required for casting the complete shaft. The very slow casting of the shaft is due to the large cake thickness and the use of a solid mould where the filtration area equals the small cross-sectional area of the shaft.

In order to reduce the casting time, spin test discs were also cast using a partially flocculated slip. In this case, only 0·03 wt% PEI was added to keep the interparticle interaction at a low and more controlled level. By using a partially flocculated slip, the time for casting a spin test disc could be reduced to about half the time required when using a stabilized slip, see Fig. 15. This reduction in casting time can be very essential when considering the economic aspects of large scale production of these kinds of components. In general, the partially flocculated slips gave an increased plasticity of the green bodies, compared to using the stabilized slips. The increased plasticity promoted the resistance to crack formation, but on the other hand, the adherence to the solid mould became worse, which made the demoulding more difficult. Also in this case, the best results were achieved at relatively low maximum pressures, less than 1·0 MPa. As mentioned earlier, the thixotropy of the partially flocculated slip had to be controlled (by extra addition of polyacrylic acid) to avoid processing problems, such as clogging of slip tubes and valves.

However, by using properly adjusted pressure schedules as well as demoulding procedures, complete spin test discs without cracks could be obtained from both the stabilized and the partially flocculated slips. Photographs of pressure cast spin test discs are seen in Fig. 16.

5 Discussion

It has been shown that high-performance ceramic materials, such as Si_3N_4, can be pressure slip cast using commercial moulds, with a pore size 30–40 times larger than the particle size. Figure 17 summarizes the factors which were found to have the main influence on the consolidation behaviour of Si_3N_4 slips, but the results can of course also be extended to other powder systems.

First of all, the risk of penetration increases with the decrease in particle size. It is for instance, much easier to consolidate the KemaNord powder used in this study with a relatively wide particle size distribution, than a Si_3N_4 powder with finer particle sizes and a more narrow particle size distribution, as, for instance, the UBE-E10 powder. The particle size distribution and the powder morphology also determine the solid loading of the slip, and it has been shown that it is an advantage if a high solid loading can be obtained while still having low slip viscosity. With the powder used in this study, much higher solid loadings (above 42 vol.%) can be reached compared to many other commercial Si_3N_4 powders. However, sometimes a submicron powder as the UBE-E10 powder is required due to its very good sinterability. In this case it is necessary to increase the attractive particle forces by introducing a partial flocculation, in order to obtain an adequate consolidation. A partial flocculation also increases the casting rate, which can be an added advantage.

The above factors can also be expressed in rheological terms, i.e. a slip for pressure casting should have pseudoplastic properties in order to

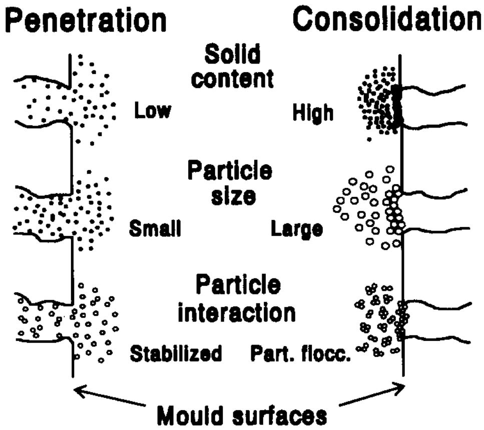

Fig. 17. Schematic illustration of the factors affecting the consolidation behaviour in pressure casting with Si_3N_4 slips. The pore size of the filter material is about 20–30 μm whereas the particle size is <1–2 μm.

be suitable for casting. This pseudoplastic behaviour can be introduced by increasing the solid content and/or introducing a slight instability of the slip. Both these techniques will increase the particle interaction and hence promote the consolidation. It is also important to adjust the pressure cycle according to the rheological properties of the slip. When the slip has a pseudoplastic behaviour the rate of the initial pressure increase should be slow. A slow pressure increase corresponds to low shear rates, where the viscosity of the slip is high and it will be more difficult for the slip to penetrate the mould. At a faster rate of pressure increase, corresponding to shear rates where the viscosity of the slip is low, the risk of slip penetrating the mould surface will be more pronounced.

When the solid loading of a slip is increased or the slip is partially flocculated, the viscosity level will of course be higher. Increased viscosity will make it more difficult to remove defects by sieving, and most often a coarser sieve has to be chosen. In this study a 50 μm sieve was used for the stabilized slip, whereas it had to be changed to 90 μm when sieving the partially flocculated slips or slips with very high solid loadings. Consequently, the risk of introducing larger defects in the material will increase.

The use of stabilized slips has many advantages. First of all, by using stabilized slips, soft agglomerates are easily broken and the primary particles can be kept apart by repulsive forces. This means that the sintering additives will be effectively dispersed in the system. Stabilized slips also have more stable long-term properties than the flocculated slips, and hence large batches of the slip can be prepared, which can be used (and re-used) even after several weeks.

In order to obtain a good deagglomeration and milling of the powders, the slips in this study were first stabilized and ball-milled before the partial flocculation was introduced by the addition of polyethyleneimine. There will of course be other ways to introduce the flocculation, such as for instance by decreasing the pH, adding electrolytes or choosing another type of flocculant. Experiments were also conducted in which the interparticle forces were increased by decreasing the pH. The polyacrylic acid will be less dissociated at lower pH values, and hence, less negatively charged and not as effective in stabilizing the particles.[11] When the pH was decreased in steps from pH 9·4 to pH 7·8 the flocculation increased, and results similar to those achieved when using PEI additions were obtained. However, the addition of PEI seemed to be easier to control in large-scale slip preparation and it was chosen for the subsequent experiments. As shown later in the study, the technique used to introduce a partial flocculation was not optimized. The partially flocculated slip also became thixotropic which gave practical problems with clogging of tubes and valves in the large-scale pressure casting experiments. More detailed rheological studies are needed to optimize the particle interaction of the destabilized slip and to control the obtained floc structure (type and strength). With the controlled, very limited flocculation used in this study, no inhomogeneities or density gradients could be detected in the cast compacts. Thus, the floc structure did not break down during the consolidation, not even when the pressure gradient over the consolidated layer was large. Consequently, if there existed certain compressibility of the consolidated bodies it must have been of reversible nature.

A mould with a finer pore size than in the commercial mould materials could, of course, be used in order to reduce the risk of slip penetration. However, this is probably not realistic, because the cleaning of the mould would be much more difficult and the risk of particles clogging the pores in the mould would increase. Furthermore, the filtration resistance of the mould could then no longer be neglected, which would make the whole casting process slower.

In filter pressing, a cylindrical uniform consolidated layer is formed and the casting rate as well as the whole consolidation process can be controlled and determined in an accurate way. In the unidirectional casting of the cones, the filtration area changes during the casting process, becoming continuously smaller, and hence, the casting time will be more difficult to predict. Even more difficult to control is the casting of the spin test disc when the casting is a modified unidirectional casting with the consolidated layers initially formed simultaneously at both the top (plane surface) and the curved surface in the porous mould. In practice, the results from the initial filter pressing experiments give a first indication of what casting times to expect when casting in the machine. Some pre-casting experiments will therefore be required to determine the actual casting time needed to complete the casting of a more complex component. A possibility to better control the casting process *in situ*, is to use microfocus X-ray radiography or ultrasonic techniques.[12,13] The in-process monitoring of the slip/cast solid interface will also facilitate the ability to apply constant casting rates for more complex-shaped components.

As shown in this study, the design of the mould is very critical for the obtained result. It is not only the presence of relief angles which are important, but also to determine if the mould should consist of one or two porous mould parts, and how the consolidation should proceed. The design of the spin test disc mould was not optimal because critical stresses arose in the cast component. A new mould will therefore be constructed for the next generation of pressure cast spin test discs.

Lange & Miller[4] have reported difficulties in demoulding pressure slip cast components due to dilatancy of the green bodies which made them flow slightly after the release from the mould. The only tendency to dilatancy of the cast compacts observed in this study, was when very low maximum pressure was used (less than 0·3–0·4 MPa). It has also been shown in pressure casting of other systems, for instance, oxide materials, that the problems with dilatancy of green bodies can be avoided by increasing the casting pressure. It is interesting to note that the plasticity of the green compacts not only is determined by the rheological behaviour of the slip, but also by the pressure used in the casting process. In the pressure casting of the complex spin test discs some plasticity of the cast component (i.e. green body stress relaxation) was desirable, because this improved the ability to withstand stresses.

The maximum pressure that can be used in practice is highly dependent on the type of component to be cast and the design of the mould. For the 'thicker' cone with good relief angles there were no problems in the use of pressures up to 4·0 MPa. In order to obtain enough plasticity and a minimum of stresses, the casting of the more complex-shaped spin test discs has to be performed at a pressure lower than 1·0 MPa. This was at least true for the mould design used in this study.

The drying of a thick complex-shaped component is also a critical step which needs to be performed in an accurate way to avoid cracking.

To conclude, the goal for the continued research will be to develop a more 'robust' system in order to obtain less crack-sensitive compacts and to make it possible to use pressure schedules which favour faster castings. This includes both further optimization of the rheological properties of the slip and improvement of the mould design.

6 Conclusion

Components in silicon nitride have been produced by pressure slip casting using commercial porous polymeric moulds. The penetration of the slip into the mould can be avoided by optimization of the slip properties (particle size distribution, solid content and particle interaction) as well as by the pressure schedule used. Thick components (above 50 mm) were unidirectionally pressure slip cast from a stabilized slip, without obtaining any critical inhomogeneities or gradients in the cast body. For complicated components, the design of the mould and the green body stress relaxation are critical factors which have to be considered in order to avoid crack formation during demoulding and drying. The green body relaxation, i.e. green body plasticity, was controlled by the degree of stability and the casting pressure. Crack-free spin test discs were pressure slip cast from stabilized slips in 3·5 h. With partially flocculated slips the casting time could be reduced two- to threefold, compared to using highly stabilized slips. However, the rheology of the partially flocculated slips has to be better controlled; otherwise, the thixotropic behaviour can cause problems in large scale pressure slip castings processes.

Filter pressing experiments have proven to be an excellent technique to simulate pressure slip casting in laboratory scale and to evaluate and optimize the casting properties of various slips. A model for the consolidation process in filter pressing, which can be adapted to all kinds of pressure schedules, was constructed and used in the characterization of the slips.

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