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Pressure Casting of Silicon Nitride

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Abstract

This report describes the consolidation behaviour of Si_3N_4 dispersions during pressure casting. Dispersions of two Si_3N_4 powders were uni-dimensionally pressure cast at different pressure levels, up to 8 MPa, both in a flocculated and a deflocculated state. The flocculated slips resulted in much more compressible cakes, with lower specific hydrodynamic resistances compared to the deflocculated slips. The porosity of a flocculated consolidated layer was always higher than that of a deflocculated layer, even when much higher pressures had been used to form the flocculated cake. This type of compressible cake became conical after drying. It was shown that dispersions with a dilatant behaviour result in products with higher porosities at higher pressures.

The quadratic equation describing the filtration process was also valid when a compressible consolidated layer was processed. From the Kozény–Carman equation a specific permeability surface area was calculated. For the deflocculated cakes this specific permeability surface area was in good agreement with the measured BET specific surface area when the Kozény constant was taken to be 5.

Diese Arbeit beschreibt die Scherbenbildung von Si_3N_4-Dispersionen während des Druckschlickergießens. Dispersionen zweier Si_3N_4-Pulver wurden eindimensional bei diskreten Drücken bis maximal 8 MPa sowohl in flockuliertem wie auch in nicht flockuliertem Zustand druck-schlickergegossen. Verglichen mit den deflockulierten Schlickern ergaben die flockulierten Schlicker nachverdichtbarere Filterkuchen mit einem geringeren hydrodynamischen Widerstand. Die Porosität der aus flockuliertem Schlicker hergestellten Schichten war, auch bei Anwendung eines erheblich höheren Druckes, immer höher als diejenige der aus nicht flockuliertem Schlicker hergestellten Schichten. Derlei konsolidierte Kuchen zeigten nach dem Trocknen eine konische Form. Es konnte nachgewiesen werden, daß dilatante Dispersionen bei höheren Drücken Kuchen höherer Porosität bilden. Die zur Beschreibung des Filtrationsprozesses üblicherweise verwendete quadratische Gleichung konnte auch auf das Druckschlickergießen angewendet. Aus der Kozény–Carman Gleichung wurde eine spezifische Permeabilitäts–Oberfläche berechnet. Bei einer Kozény–Konstanten von 5 stimmt diese spezifische Permeabilitätsoberfläche für die deflockulierten Kuchen gut mit der gemessenen spezifischen Oberfläche nach BET überein.

On décrit ici le comportement en consolidation de suspensions de Si_3N_4 lors de leur coulage sous pression. On a coulé de façon uni-dimensionnelle à différentes pressions (jusqu'à 8 MPa), des suspensions de deux poudres de Si_3N_4, à l'état flocculé ou déflocculé. Par comparaison avec les suspensions déflocculées, les suspensions flocculées conduisent à des tessons bien plus compressibles, possédant des résistances hydrodynamiques spécifiques plus basses. La porosité des couches consolidées à partir de l'état flocculé est toujours supérieure à celles des couches consolidées à partir de l'état déflocculé, même lors de l'emploi de pressions bien plus hautes. Ce type de tesson compressible devient cônique après le séchage. On montre que les suspensions qui présentent un caractère dilatant conduisent à des produits à porosité plus élevée lorsque la pression de coulage est accrûe.

L'Equation quadratique qui décrit le processus de filtration est également valable dans le cas de la consolidation de couches compressibles. On a calculé la surface de perméabilité spécifique à partir de l'équation de Kozény–Carman. Dans le cas de tessons déflocculés, la valeur de cette surface de perméabilité spécifique est en bon accord avec les surfaces spécifiques mesurées par BET lorsque la constante de Kozény est égale à 5.

Notation

V_f is the filtrate volume, both in and below the filter (m^3),
t is time (s)

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P is the effective filtrating pressure (Pa)
c is the Kozény constant
V_d is the dispersion volume (m^3),
A is the filtrating surface area (m^2),
L is the thickness of the cake (m),
F is the total force on the piston (N),
F_f is the opposing force on the piston due to friction with the cylinder wall (N),
α is the specific cake resistance (m^{-2}) (equals the reciprocal of the permeability (m^2)),
ϕ is the volume fraction of solids in the dispersion,
ε is the wet porosity of the consolidated layer (i.e. the porosity in the as-cast state),
η is the viscosity of the dispersion medium (Pa . s),
R' is the resistance of the filtering medium (m^{-1}), and
x is the displacement of the piston (m).

1 Introduction

Silicon nitride is a structural ceramic material, still gaining in interest because of its good mechanical and chemical properties over a wide temperature range. Because of the increase in sinterability with decreasing particle size, the particle size of commercially available Si_3N_4 powders is getting smaller. As a result of this reduction in particle size, the forming of ceramics often becomes more difficult.

Forming of ceramics can be accomplished by several different techniques. Colloidal processing of ceramic powders results in more homogeneous packing of the particles in comparison with 'dry' techniques.[1] A homogeneously packed compact will exhibit a desired uniform sintering behaviour.

Pressure casting is a relatively new 'wet' forming method, comparable with slip casting, in which dewatering is achieved by filtration. An advantage of slip and pressure casting is that they are suitable techniques for making products with difficult geometries. Unlike slip casting, in which the filtration originates from the capillary action of plaster of Paris, pressure casting derives its driving force from an external pressure applied to the ceramic suspension. This results in an increased rate of cake formation[2] in pressure casting. Another advantage of pressure casting over slip casting is the better reproducibility of the product dimensions due to the use of polymeric moulds, which show no wear, instead of plaster moulds, which do.

The compressibility of cakes, resulting from pressure casting, is important because of a possible change in hydrodynamic resistance and porosity with a change in pressure. This may negatively affect the gain in casting time at higher pressures. In the theory of slip casting, the assumption that the cake is incompressible may be justifiable. Low pressure differences of c. 0·1 MPa are typical for slip casting. However, in pressure casting, with pressure differences up to 8 MPa, this assumption may be unrealistic.

The highest density of a green product after slip casting can be obtained with completely deflocculated slips, whereas flocculated slips result in green products with a lower density.[1] Pressure casting of a flocculated slip results in a more dense green product when higher pressures are applied.[1] The object of interest in the present investigation was the behaviour of Si_3N_4 slips. Slips of two different Si_3N_4 powders were pressure cast at a constant pressure, both in a deflocculated and flocculated state. These pressure casting experiments were performed at different pressure levels. The pressure dependence of the hydrodynamic resistance, the porosity of the green product and the drying shrinkage were measured.

2 Theory

The pressure casting experiments were performed in a laboratory pressure casting unit, which is schematically shown in Fig. 1. At constant pressure the

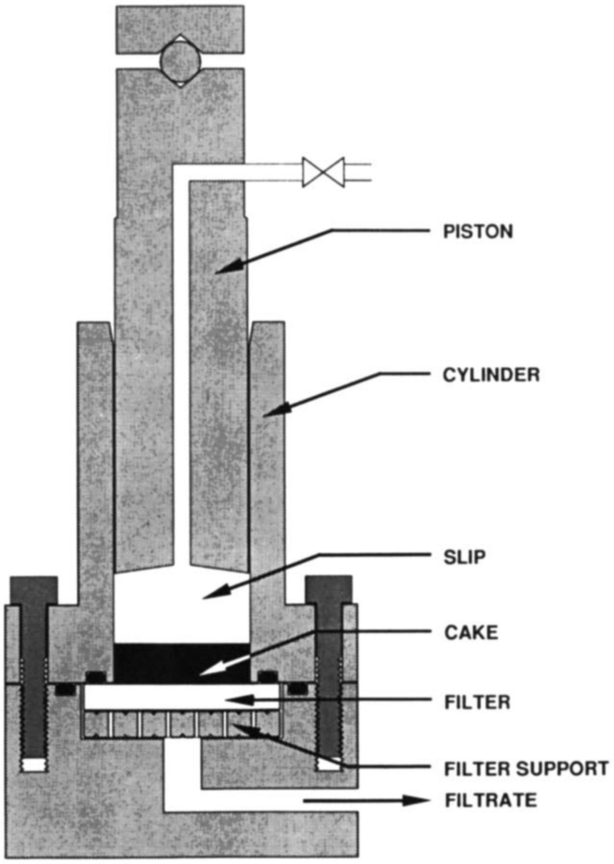

Fig. 1. Drawing of the laboratory pressure casting unit. The drawing is to scale with an inner diameter of the cylider of 50 mm.

displacement of the piston (x) was recorded as a function of the time (t).

The fluid flow through a porous system is described by Darcy's law:[3]

$$\frac{dV_f}{dt} = \frac{A\,.\,P}{\eta\,.\,(\alpha\,.\,L + R')} \tag{1}$$

For uni-dimensional filtration the following balances hold:

A solids mass balance:

$$\phi\,.\,V_d = (1 - \varepsilon)\,.\,A\,.\,L \tag{2a}$$

and two filtrate volume balances:

$$(1 - \phi)\,.\,V_d = \varepsilon\,.\,A\,.\,L + V_f \tag{2b}$$

$$V_f = A\,.\,x \tag{2c}$$

For the effective filtrating pressure P holds:

$$P = (F - F_f)/A \tag{3}$$

After elimination of V_d, V_f, L and P from eqns (1), (2) and (3), eqn (1) can be integrated with boundary condition $x = 0$ when $t = 0$, which results in eqn (4):

$$t = a_1\,.\,x + a_2\,.\,x^2 \tag{4a}$$

$$a_1 = \frac{\eta\,.\,A\,.\,R'}{F - F_f} \tag{4b}$$

$$a_2 = \frac{\eta\,.\,\alpha\,.\,\phi\,.\,A}{2\,.\,(1 - \varepsilon - \phi)\,.\,(F - F_f)} \tag{4c}$$

At the beginning of each experiment there is a small time interval in which the applied force is raised to a constant value. In this time interval filtration already takes place, but for applicability of eqn (4a) $t = 0$ has to be chosen at a moment where F is constant. This initial effect can be dealt with when R' is defined as a sum of several resistances:

$$R' = R_p + R_m + R_c \tag{5}$$

where

R_p is the resistance of the porous polymeric material (m^{-1}),

R_m is the resistance of the membrane, covering the polymeric filter (m^{-1}), and

R_c is the resistance of the initial cake which has already formed at $t = 0$ (m^{-1}).

Tiller[4] showed that, at constant pressure filtration, eqn (4a) is also valid for compressible cakes when the assumption is made that the shape of the pressure profile over the cake does not change with filtration time. In this case ε and α in eqn (4c) are the average wet cake porosity and average specific resistance over the total thickness of the cake.

Kozény and Carman derived an expression in which α is related to the wet cake porosity and the specific permeability surface area (S_p) of the powder:[3,4]

$$\alpha\,.\,\varepsilon^3 = c\,.\,(1 - \varepsilon)^2\,.\,S_p^2 \tag{6}$$

where c is the Kozény constant that contains the shape factor and tortuosity of the flow channels. Usually c is taken to be 5.[3,4] For the powders investigated, the calculated value for S_p from expression (6) can be compared with the BET surface (Table 1). Note that S_p (m^2/m^3) and S_{BET} (m^2/g) have different dimensions:

$$S_p = 10^3\,.\,\rho\,.\,S_{BET} \tag{7}$$

where ρ is the density (kg/cm^3) of the consolidating material.

3 Materials and methods

For the pressure casting experiments several Si_3N_4 slips were prepared. As dispersing medium doubly distilled water was used. The silicon nitride powders used were LC-12 and SN-E-10, of which the characteristic data are summarized in Table 1. A deflocculated as well as a flocculated slip was prepared of both powders.

For the deflocculated LC-12 slip with a solids content of 32 vol.%, Na_2SiO_3 (p.a.) was used as a deflocculant (0·6 wt%, based on ceramic content). For good deagglomeration, portions of 100 cm³ slip were treated ultrasonically for 6 min (Branson Sonifier 250, Branson Ultrasonics Corp., Shelton, CT, USA; power consumption 175 W). The flocculated LC-12 slip of 18 vol.% was prepared by dispersing the powder in doubly distilled water, without any deflocculant and without ultrasonic treatment.

The deflocculated SN-E-10 slip of 32 vol.% was prepared by dispersing the powder in doubly

Table 1. Investigated Si_3N_4 powders

Powder	*LC-12*[a]	*SN-E-10*[b]
BET (m^2/g)[c]	21	9
d_{90} (μm)[d]	1·0	0·8
d_{50} (μm)[d]	0·4	0·4
d_{10} (μm)[d]	0·1	0·2
Fabrication process	Nitridation of silicon	Decomposition of silicon diimide

[a] Hermann C. Starck, Berlin, FRG.
[b] UBE Industries Ltd, Tokyo, Japan.
[c] Flowsorb II 2300, Micromeritics, Norcross, USA.
[d] Sedigraph 5100, Micromeritics. Norcross, USA.

distilled water. This slip was also treated ultrasonically for 6 min. No deflocculant was needed to get a stable deflocculated SN-E-10 slip. Na_2SiO_3 had no positive effect on the deflocculation of SN-E-10. The flocculated SN-E-10 slip of 18 vol.% was prepared from the deflocculated SN-E-10 slip, by dilution, under mild stirring, according to the following scheme:

100 volume parts of deflocculated SN-E-10 slip,
68·5 volume parts of water, and
20 volume parts of a saturated $Al(NO_3)_3$ solution.

In the laboratory pressure casting unit, shown schematically in Fig. 1, these four slips were pressure cast at five different pressure levels (0·5, 1, 2, 4 and 8 MPa) at room temperature. Since the available porous polymeric material (Gebrüder Netzsch Maschinenfabrik GmbH & Co., Selb, FRG) did not have the desired small pore size, it was covered by a membrane (Versapor 0·45 μm, Gelman Sciences Inc., Ann Arbor, MI, USA). In this way, the produced specimen were disks with a diameter of 50 mm and a thickness between 10 and 15 mm.

The pressure casting unit was placed between the clamps of a mechanical testing machine (Precision Universal Testing Machine 200 kN, ESH Testing Ltd, West Midlands, UK). The friction force (F_f) on the piston was measured with an empty casting unit at different displacement speeds and was found to be around 50 N. In a casting experiment, the load (F) was applied within 5 s and the displacement of the piston (x) was recorded as a function of the time (t). Then eqn (4a) was fitted to these data by a least-squares fitting procedure which produced the coefficients a_1 and a_2. With a_2 and $\eta = 1$ mPa . s. α could be calculated with eqn (4c), after ε was measured. ε was determined by measuring the weight difference of the cake before and after drying. The cakes were allowed to dry from all sides. After drying, the relative linear shrinkage in diameter of the cakes was measured. The densities of the dried cakes were measured by Hg-porosimetry (Pore Sizer 9310, Micromeritics, Norcross, USA).

4 Results and discussion

4.1 General

The produced wet cakes from the deflocculated slips could all be handled very easily, but the flocculated wet cakes had to be handled with care, because of a very poor strength.

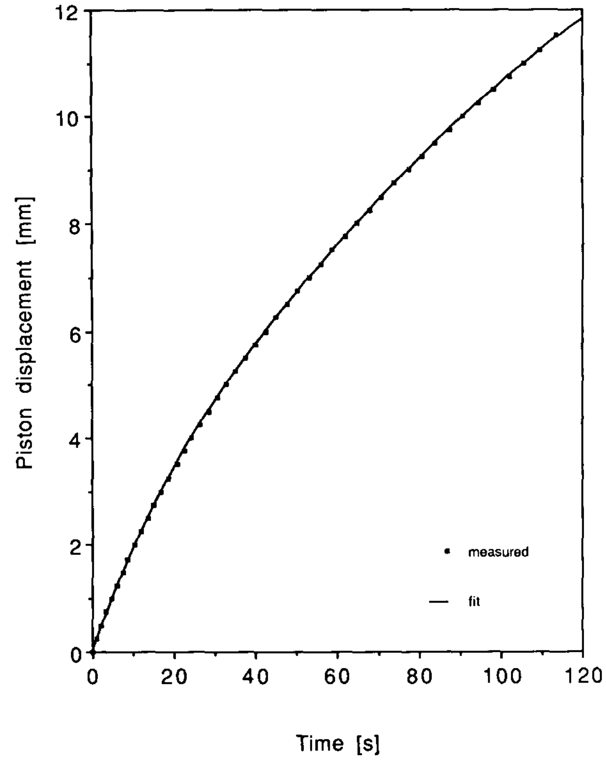

Fig. 2. Piston displacement (x) as a function of time (t) during the pressure casting experiment of the flocculated LC-12 slip at 8 MPa. Fit parameters: $a_1 = 4{\cdot}039$ s/mm, $a_2 = 0{\cdot}509$ s/mm^2.

To prevent crack formation, the wet disks from LC-12 had to be dried very carefully (at room temperature over several days), while SN-E-10 products could be dried very quickly at 120°C over a few hours.

Equation (4a) showed a good fit with all the x–t curves. One set of data points, together with the fitted curve, is shown in Fig. 2. The accuracy of a_2 was better than 0·7% for all experiments and did not show a pressure dependence.

4.2 Porosity and shrinkage

The wet and dry porosities of the different systems are plotted as a function of the casting pressure in Figs 3 and 4. With LC-12 it is shown that the wet porosity decreases with increasing filtration pressure; the flocculated system having the highest pressure dependence. This behaviour was expected: in a flocculated system more flocs will be broken when a higher pressure is applied. After drying, the remaining porosity is pressure independent, and the state of deflocculation determines which end porosity is reached. Samples resulting from flocculated suspensions have a higher porosity than products from deflocculated slips. Therefore the green density of a cast body from a flocculated slip cannot reach the green density of a product from a deflocculated slip by increasing the pressure.

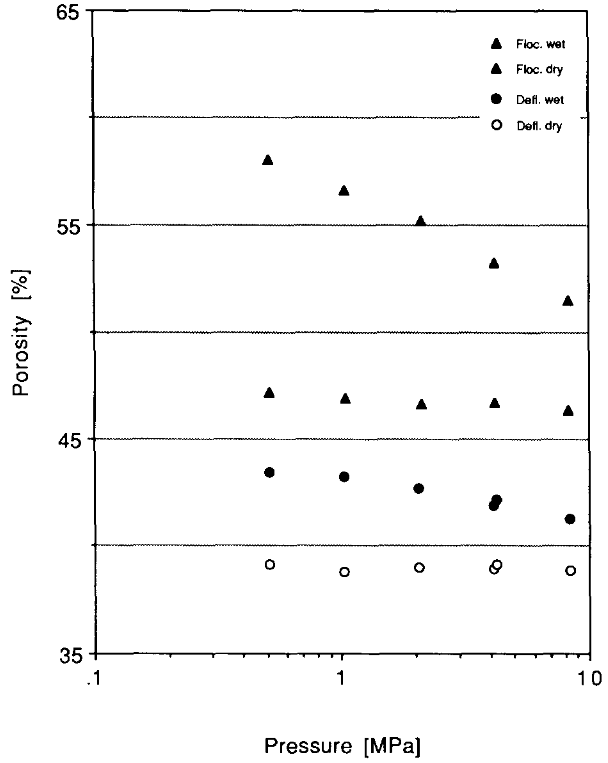

Fig. 3. Wet and dry porosities of flocculated (Floc.) and deflocculated (Defl.) LC-12 cakes as a function of the casting pressure.

The average linear shrinkage, measured from the diameter of the LC-12 disks, is shown in Fig. 5 as a function of the forming pressure. The difference between wet and dry porosities, which is a measure for the volumetric shrinkage, and the measured linear shrinkage both show quantitatively the same pressure dependence. The shrinkage of the LC-12 products becomes less at higher pressures, with the largest shrinkage for products from a flocculated suspension.

The SN-E-10 curves for porosity and shrinkage (Figs 4 and 5) show a less clear view. The wet porosity of disks from the flocculated system decreases when the pressure is increased. This effect was expected, but the dry porosity exhibits a strange behaviour. The shrinkage of the disks expected from the difference between the wet and dry porosity is smaller than the one measured from the diameter. The wet porosity is sometimes even smaller than the dry one, which suggests that there is an expansion instead of a shrinkage during the drying process. This effect might be caused by strain relaxation of the consolidated layer after it is ejected from the cylinder, a phenomenon which was already described by Lange & Miller.[1] In that case there is an expansion of the disk in the early drying stage, and when this strain relaxation occurs predominantly in the direction perpendicular to the filtering surface,

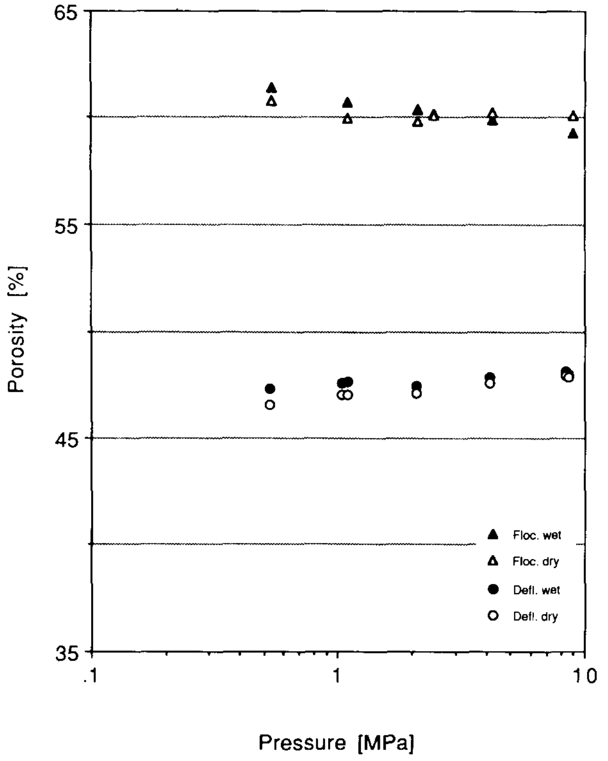

Fig. 4. Wet and dry porosities of flocculated (Floc.) and deflocculated (Defl.) SN-E-10 cakes as a function of the casting pressure.

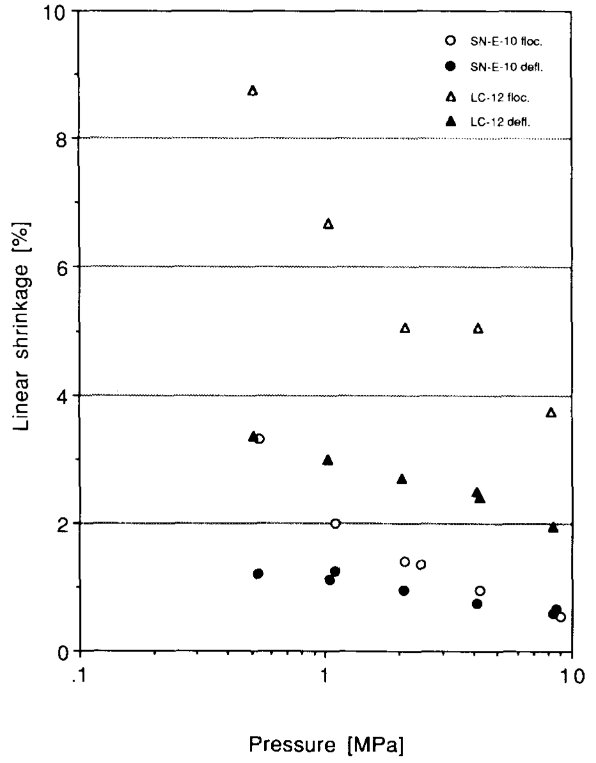

Fig. 5. Average linear shrinkage in diameter of LC-12 and SN-E-10 cakes, flocculated (floc.) and deflocculated (defl.), as a function of the casting pressure.

the dry porosity can be higher than the wet porosity, still with a shrinkage in the diameter. This strain relaxation may cause a discrepancy between the measured wet porosity and ε in eqns (4c) and (6).

In the case of the deflocculated SN-E-10 system it is striking that the porosity increases with the applied pressure. This was not observed in the other three systems. An explanation for this may be found in the rheological behaviour of the deflocculated SN-E-10 slip. This slip has a slightly dilatant behaviour, caused by a volumetric solids content which is close to the maximum solids content. As a result of dilatancy, cluster formation[5] takes place at high shear rates and these clusters will be built-in in the consolidated layer. Because the shear rate increases with increasing consolidation rate, more structure will be built in at higher pressures. In this way the increase of the wet porosity for the deflocculated SN-E-10 system is explained.

The shrinkage of the deflocculated SN-E-10 system shows the same behaviour as all the other systems: the shrinkage decreases as the pressure is increased (Figs 4 and 5). It seems strange that a more porous cake shows less shrinkage, but it may be caused by the presence of more clusters in the product.

The porosities of the SN-E-10 cakes are larger than those of the LC-12 cakes, because of the more narrow particle size distribution of SN-E-10. In addition, SN-E-10 cakes shrink less than LC-12 cakes. The larger shrinkage of LC-12 cakes is probably caused by the smaller pores in these products. Scherer[6] explained that smaller pores exhibit a larger stress during the drying process. In the case of the LC-12 cakes the shrinking stress is large enough to reach the lowest possible porosity for a given degree of deflocculation, so the dry porosity is independent of the casting pressure.

4.3 Shape of the products

All the disks made by pressure casting had a conical shape (Fig. 6). The top diameter was smaller than that at the bottom (in contact with the filter). This can be understood if the pressure gradient over the cake is taken into account. The effective network pressure has the largest value at the bottom and is zero at the top part of the cake.[7] From Fig. 5 it is clear that the shrinkage is larger when the pressure is lower. So, the top of the cake will shrink more than the bottom part. The conical shape was most extreme for LC-12 flocculated cakes, followed by SN-E-10 flocculated, LC-12 deflocculated and the least with SN-E-10 deflocculated cakes.

With respect to the deflocculated SN-E-10 slip, another mechanism may be responsible. At the beginning of an experiment the filtration rate is higher than at the end, and so will be the shear rate. In the case of the deflocculated SN-E-10 slip this will cause more structure build-up in the cake at the beginning of the experiment than at the end. The previously mentioned observation that more structure build-up gives rise to less shrinkage, could also explain the conical shape of the dry deflocculated SN-E-10 cakes.

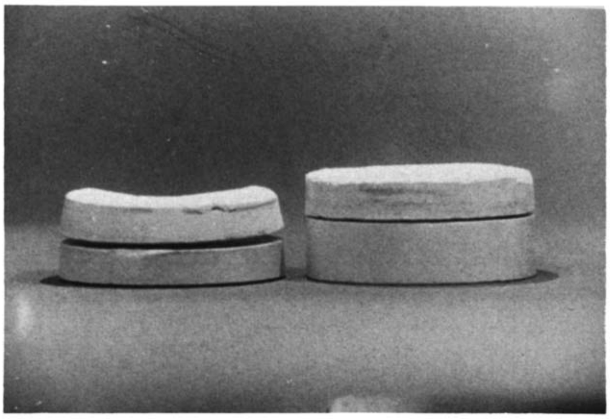

Fig. 6. Disks made by pressure casting of flocculated LC-12 slip (upper left), deflocculated LC-12 slip (lower left), flocculated SN-E-10 slip (upper right) and a deflocculated SN-E-10 slip (lower right).

The conical shape of all samples could be reduced by subjecting the whole consolidated body to the same network pressure. This was achieved by compression of the cake after the forming process: the remaining slip was poured off and a filter was placed on top of the cake. Then the piston was put back in place and the same load as in the forming process was applied.

4.4 Specific hydrodynamic resistance

The specific resistance (α) calculated from a_2 in eqn (4) is shown as a function of the pressure in Fig. 7. The value of α of the LC-12 deflocculated cakes is weakly pressure dependent. It can be concluded that the LC-12 deflocculated consolidated layer is slightly compressible. This compressibility is affirmed by the decrease of the wet porosity of the LC-12 deflocculated cakes with increasing pressure. The pressure dependence of α, however, gives a better indication of the compressibility than does the pressure dependence of the wet porosity. This is because α is measured during the consolidation process, and the wet porosity is measured when there is no pressure on the cake, which allows a possible strain relaxation of the cake.

The value of α of the flocculated LC-12 cakes is smaller and more pressure dependent than that of

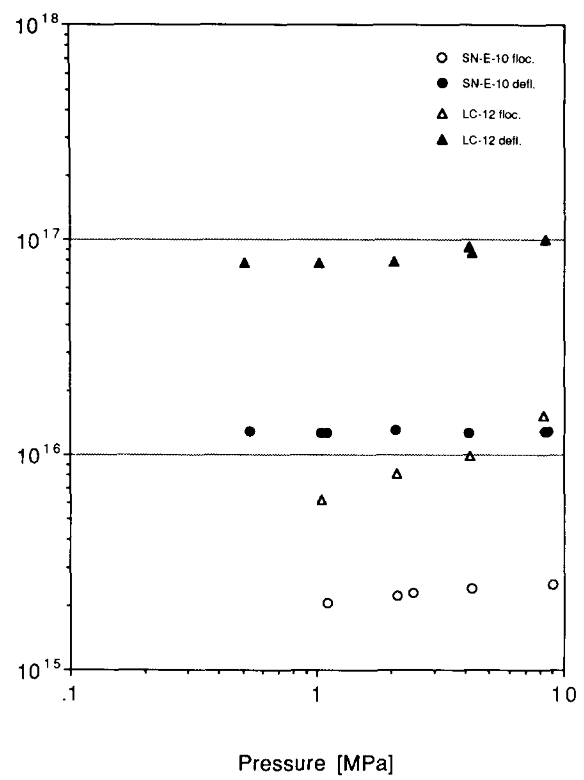

Fig. 7. Average specific resistance (α) of LC-12 and SN-E-10 flocculated (floc.) and deflocculated (defl.) cakes as a function of the casting pressure.

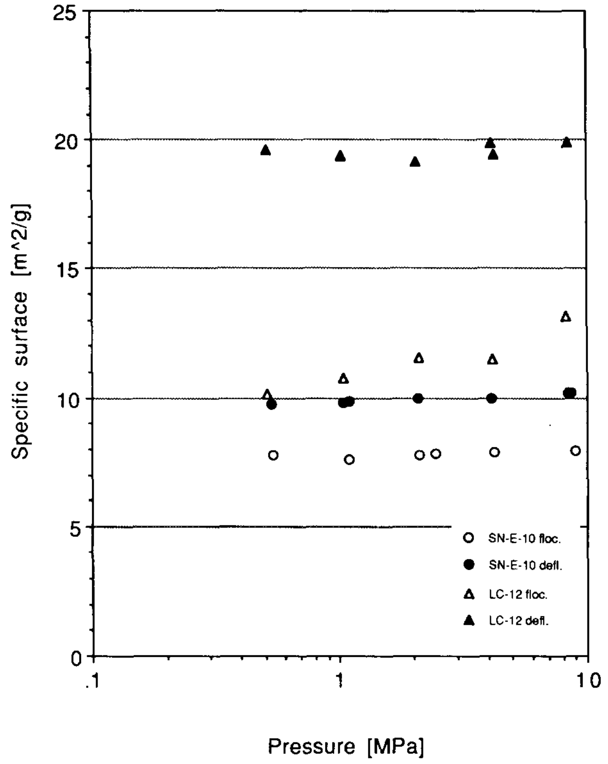

Fig. 8. Specific permeability surface area (S_p) of LC-12 and SN-E-10 flocculated (floc.) and deflocculated (defl.) cakes as a function of the casting pressure.

the deflocculated LC-12 cakes. This larger compressibility and lower resistance was expected for a flocculated system and was already shown by the pressure dependence of the wet porosity.

The value of α of the deflocculated SN-E-10 system does not show a pressure dependency. This in contrast with the slight increase of the wet porosity with increasing pressure. The uncertainty in α is probably too large to exhibit such a weak pressure dependence.

The pressure dependence of α of the flocculated SN-E-10 system is as expected, i.e. α increases as the pressure increases. This increase is in agreement with the decrease of the wet porosity with increasing pressure. The specific resistance of the flocculated cakes was smaller than α of the deflocculated SN-E-10 cakes, as was expected.

4.5 Specific permeability surface area

Kozény and Carman showed that α is a function of ε and of the specific permeability surface area (S_p). This Kozény–Carman equation is applied to the deflocculated as well as to the flocculated system with the assumption of the Kozény constant (c) being 5 in both cases, and S_p being the only variable. With the measured values of α and ε, S_p could be calculated from eqn (6). S_p is shown as a function of the pressure in Fig. 8, for the different systems, with its dimension adapted to the unit of the BET specific surface area (m^2/g). It is striking how well the calculated values for S_p of the deflocculated cakes resemble the values from the BET measurements (Table 1). S_p of the flocculated cakes is slightly lower. This is probably caused by the fact that the liquid flow is primarily through the pores between the flocs and not through the flocs. S_p of the flocculated LC-12 cakes increases clearly with increasing pressure, which indicates the breaking of flocs at higher pressures.

5 Conclusions

The performance of Si_3N_4 slips during pressure casting has been evaluated. The results show that Darcy's law and the Kozény–Carman equation are fully applicable in describing the pressure filtration of flocculated and deflocculated slips. However, with flocculated systems the specific permeability surface has to be adapted because of preferential flow channels.

The specific resistance α is more pressure dependent for LC-12 slips compared to SN-E-10 slips and more pressure dependent for flocculated cakes. Systems with less pressure dependence of α are less compressible. This compressibility is important when mould release is considered. Systems with no compressibility will lead to products without strain relaxation and hence these products will easily release from the mould. Compressible systems, however, can lead to products with strain relaxation, due to which stresses can occur after the pressure is released. In this case, mould release will be difficult.

The wet porosity of a compressible cake decreases with increasing pressure. The dry porosity of a compressible consolidated layer will be pressure independent if the drying stress is large compared to the pressure applied during casting. In this case, the shrinkage of a compressible cake will be pressure dependent, which might result in a poorly shaped product or in a product with internal stresses. Besides being influenced by the applied pressure during casting, the porosity of a consolidated layer can also be influenced by the viscosity behaviour of the slip from which it is formed. Dilatant behaviour of a slip might cause higher porosities at higher pressures because of the higher shear rates under these circumstances. The porosity of a consolidated layer is influenced most by the degree of deflocculation of the slip. A flocculated slip will result in a more porous green product with inferior strength, compared to a deflocculated slip.

Overall it can be concluded that forming by pressure casting can be performed best with deflocculated systems. In that case the products are stronger and less compressible than in the flocculated case. From the two investigated deflocculated systems SN-E-10 is preferred as starting material for pressure casting since the forming process is fast (low α), the products exhibit almost no compressibility and the drying can be carried out very quickly without introducing cracks.

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