

Colloidal Filtration of Silicon Nitride Aqueous Slips, Part II: Slip Casting and Pressure Casting Performance

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Abstract

In a previous part, the rheological behaviour of silicon nitride aqueous slips was optimized by dispersing with TMAH up to pH 11.5 using different mixing procedures and including different concentrations of sintering aids (Al_2O_3 and Y_2O_3). In this part, the obtention of pressureless sintered silicon nitride bodies by colloidal filtration techniques is studied. The kinetics of the different compositions is studied for both slip casting and pressure casting. The pressure casting kinetics is up to 20 times faster than that of slip casting, which allows the scale-up of the process for a low cost production. The obtained green density is slightly > 58%th for slip casting and 57–55%th for pressure casting, depending on the applied pressure. This small difference does not influence sintered density. At 1750°C/2h, a final density around 96%th is obtained. The sintering conditions are studied considering the time, temperature, atmosphere and sintering bed. The best results are obtained when the sintering bed has the same composition to that of the sample to be sintered. The room temperature properties of the sintered materials show a K_{IC} value higher than 6 MPam^{1/2}, comparable to those found in the literature for pressure sintered materials.

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1 Introduction

Non-oxide ceramics and, in particular, silicon nitride, have excellent thermomechanical properties

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for structural and heat engine applications, as reported elsewhere.^{1–4} Pressure sintering methods have been used for the manufacture of dense silicon nitride parts. However, the high cost of pressure assisted sintering seriously limit the on-line application of the process. The development of economical production processes for the manufacturing of complex parts of silicon nitride for structural and heat engine applications is a challenge from a technological point of view.

In this context the use of colloidal forming processes followed by pressureless sintering are an attractive procedure for the obtention of silicon nitride parts with good mechanical properties and relatively high density.^{5,6} Slip casting is a well-recognized method for the obtention of dense, defect-free ceramics.^{7,8} On the other hand, pressure slip casting is not yet as well controlled as slip casting, but it has many clear advantages for a large-scale fabrication of complex and thicker parts.^{9–11} A basic requirement for both shaping techniques is the preparation of a stable, well-dispersed slip able to consolidate during filtration in a dense and homogeneous green body.

In the first part of this series,¹² the rheological behaviour of castable silicon nitride aqueous slips was described. The stability of the slips was studied as a function of a number of processing parameters, such as the type and concentration of deflocculant or pH-adjuster, the mixing/milling procedure and homogenization time, the presence of different concentration of sintering aids (Al_2O_3 and Y_2O_3), etc. On the basis of the rheological studies performed in the first part, this second part aims to study the parameters involved in the slip casting and pressure casting forming focusing the kinetics and the characteristics of the green casts. Pressureless sintering is studied as a function of different parameters, such as the heating schedule,

the N₂ flow, the sintering bed, etc. The relationships between rheology, casting kinetics and the characteristics of the green and the sintered samples are discussed. The results presented here are always related to the slip characteristics referred to in Part I.¹²

2 Experimental

The starting Si₃N₄ powder and the sintering aids (Al₂O₃ and Y₂O₃), were characterized in Part I, as well as the deflocculating conditions and the slip preparation methods. Compositions labelled as SN1, SN2 and SN3 consisted of pure Si₃N₄, Si₃N₄ + 3 wt% Al₂O₃ + 3 wt% Y₂O₃, and Si₃N₄ + 6 wt% Al₂O₃ + 6 wt% Y₂O₃, respectively. Aqueous slips of these compositions were prepared according to three mixing/milling procedures: A, using a high shear mixer; B, using a plastic ball mill; and C, using a centrifugal mill. The slips were prepared using tetramethylammonium hydroxide (TMAH) as pH-adjuster to a solid content of 65 wt%, which represents volume contents of 36, 36.3 and 35.8% for SN1, SN2 and SN3 compositions. Some experiments were carried out using a previously attrition milled Y₂O₃

Slip casting experiments were performed on plaster of Paris moulds prepared with a ratio of plaster to water of 100/70 to obtain solid disks with 3 cm in diameter, cylindrical bars with 0.6 cm in diameter and 8 cm in length or plates with 12×6×0.4 cm. The cast wall thickness was determined by measuring the time required to cast different slip volumes by filtering in one direction. Volumes up to 6 cm³ were cast for this test putting a non-porous open cylinder onto a plaster plate, which produced uniaxial filtering.

Pressure slip casting was performed using a laboratory uniaxial press (Gabbrielli, Italy) equipped with both displacement and pressure transducers

and a computerized data acquisition system. Figure 1 illustrates the pressure casting system used in this work. Although the system allows to operate under either constant displacement or constant pressure, all the experiments were made at constant pressure conditions. Pressure casting was performed applying different pressures, usually around 1.7, 3.4, 6.8 and 10.2 MPa. Moulds consisted of porous sintered stainless steel disks with 4.5 cm internal diameter, which were covered with filter paper for casting. It has been proven that the permeability of the filtering system is two or three orders of magnitude higher than that of the formed cake and hence, this can be neglected for kinetics calculations.

The kinetics of the casting has been quantified as a filtration process on the basis of the Darcy's equation, which allows to obtain the flux of a filtrate volume through a porous bed. By applying the mass balance to the press system, and integrating the Darcy's equation, the following equation is obtained relating the thickness of the cake (x) with casting time (t):

$$x^2 = \frac{2k\Delta p}{\eta} \left(\frac{v_0}{v_c - v_0} \right) t$$

where k is the permeability of the porous bed, η the viscosity of the suspending media, p the applied pressure, v_0 the slip density and v_c the cast density.

The green cast samples were left in air 48 h for drying and subsequently characterized. Densities were measured by Hg immersion. The as-cast density was recalculated from the dry green density considering the drying shrinkage.

Surface oxidation state was evaluated by XPS according to the procedure described in Part I for slip cast and pressure cast green samples. The analysis were made in each case for samples taken from the bulk and samples taken from the external surfaces of the pieces, that is, those in contact with the mould.

Sintering experiments were made at 1750°C under N₂ flowing atmosphere introducing the samples into a BN crucible containing different bed materials, including powder of silicon nitride, silicon nitride bed for samples coated with BN spray, and mixtures of silicon nitride with the sintering aids in the proportions corresponding to compositions SN2 and SN3.

Microstructural analysis was performed by optical and scanning electron microscopy on green and sintered specimens in order to evaluate the homogeneity of the casts obtained at different conditions. The sample preparation for SEM observations was also studied. Chemical etching was performed using an alkaline mixture at

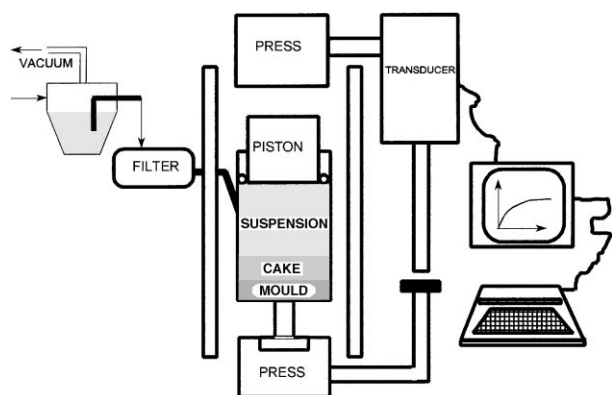


Fig. 1. Schematic representation of the pressure casting equipment.

275°C for different etching times. Plasma etching was also performed using CF_4 on polished surfaces for 40 s after treating the samples with hot N_2 for 10 min.

The behaviour of sintered samples was evaluated measuring hardness and toughness at room temperature by Vickers indentation with applied loads of 10–50 kg for 15 s.

3 Results and Discussion

3.1 Slip casting

As demonstrated in Part I, the pH value plays a critical role in the suspension stability and rheology. For this reason, the following results are referred to slips deflocculated with TMAH at $\text{pH} = 11.3 \pm 0.2$ for any composition and mixing procedure.

Figure 2 shows the cast wall thickness evolution versus casting time of the three considered compositions prepared according to mixing route B, which presented the best characteristics from a rheological point of view. The casting rate of pure SN1 compositions is faster than that of slips containing sintering aids. This fact must be related with the difficulties to maintain the desired pH. The long mixing time promotes adsorption of the TMAH but also some volatilization can occur. It

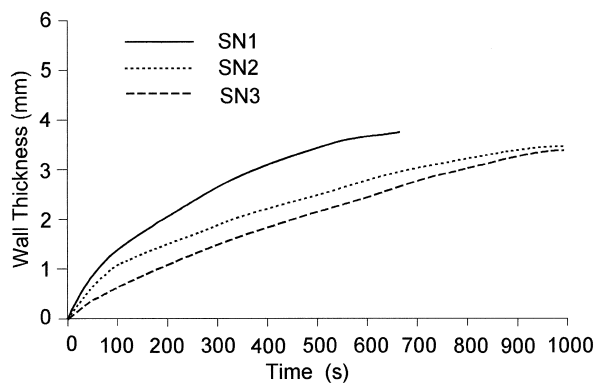


Fig. 2. Slip casting kinetics of slips prepared according to mixing route B.

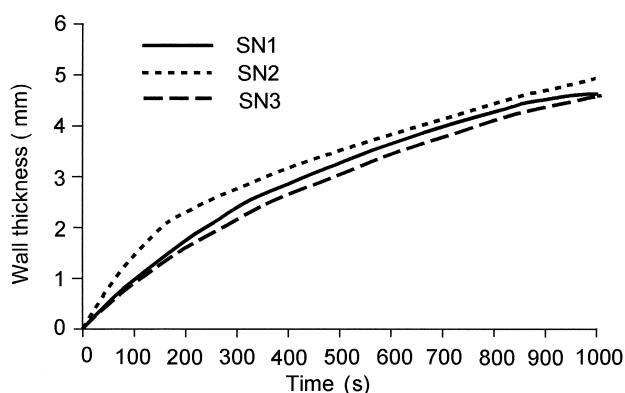


Fig. 3. Slip casting kinetics of slips prepared by mixing route C.

has been proven that when pH is readjusted before casting the resulting kinetics is similar to that obtained for the other compositions.

Similarly, Fig. 3 plots the slip casting curves of the slips prepared by homogenizing route C (centrifugal milling). In this case, a quite similar kinetics is obtained for all three compositions. Comparing with Fig. 2, it must be noted that the composition without additives SN1 exhibits the same casting rate for both mixing routes, and the differences are only observed in the slips containing sintering aids. These compositions behave similarly in each case, but the casting rate is much lower when slips are prepared by route B. This is associated with the short mixing time in route C which is not enough to assure the particles to reach an equilibrium at the surface. The final pH of the slips, just prior to casting, is summarized in Table 1. Slips prepared by route C maintain a higher pH, thus suggesting that adsorption occurs to a lower level. Taking into account the strong dependency of viscosity with pH, it could be expected that slips prepared by route C should present lower casting rates because of the higher pH. The fact that route B-slips have lower casting rates, even presenting lower pHs clearly demonstrates that a higher homogenization degree is achieved, which is in complete agreement with the rheological behaviour described in Part I.

Homogenization route A was not considered for kinetics studies due to the lower reliability and the observation of bubbles during casting.

The green densities of the slip cast samples are presented in Table 2. These values confirm the rheological and casting behaviour described before. Route B produces once more better bodies with densities higher than those obtained by the other two routes. The maximum reaches a value of near 59% th, which is quite satisfactory. The lowest densities correspond to the slips prepared by route C, as could be predicted from the rheological studies shown in the first part of this paper.

The general morphology of samples cast from slips prepared according to the different mixing procedures was observed by optical microscopy on polished surfaces after sintering at 1750°C 1h^{-1} under N_2 flow. Figure 4(a) shows a general picture of a SN2 sample prepared by route A. As can be observed, big holes due to air bubbles are always

Table 1. Final pH values of slips after mixing according to routes B and C

Composition	Mixing route	
	B	C
SN1	11	11.4
SN2	11.2	11.2
SN3	11.1	11.4

Table 2. Green densities of slip cast samples

Mixing route	A		B		C	
Composition	($g\ cm^{-3}$)	(% th)	($g\ cm^{-3}$)	(% th)	($g\ cm^{-3}$)	(% th)
SN1	1.66 ± 0.01	52.2 ± 0.3	1.78 ± 0.01	56.5 ± 0.4	1.59 ± 0.02	50.4 ± 0.7
SN2	1.72 ± 0.01	53.0 ± 0.3	1.91 ± 0.01	58.8 ± 0.1	1.69 ± 0.02	51.0 ± 0.2
SN3	1.76 ± 0.01	52.8 ± 0.3	1.93 ± 0.01	58.1 ± 0.3	1.70 ± 0.01	50.9 ± 0.5
SN2 - milled Y_2O_3	1.74 ± 0.01	53.5 ± 0.1	1.89 ± 0.01	58.1 ± 0.3	—	—

Theoretical densities ($g\ cm^{-3}$): SN1, 3.18; SN2, 3.25; SN3, 3.33.

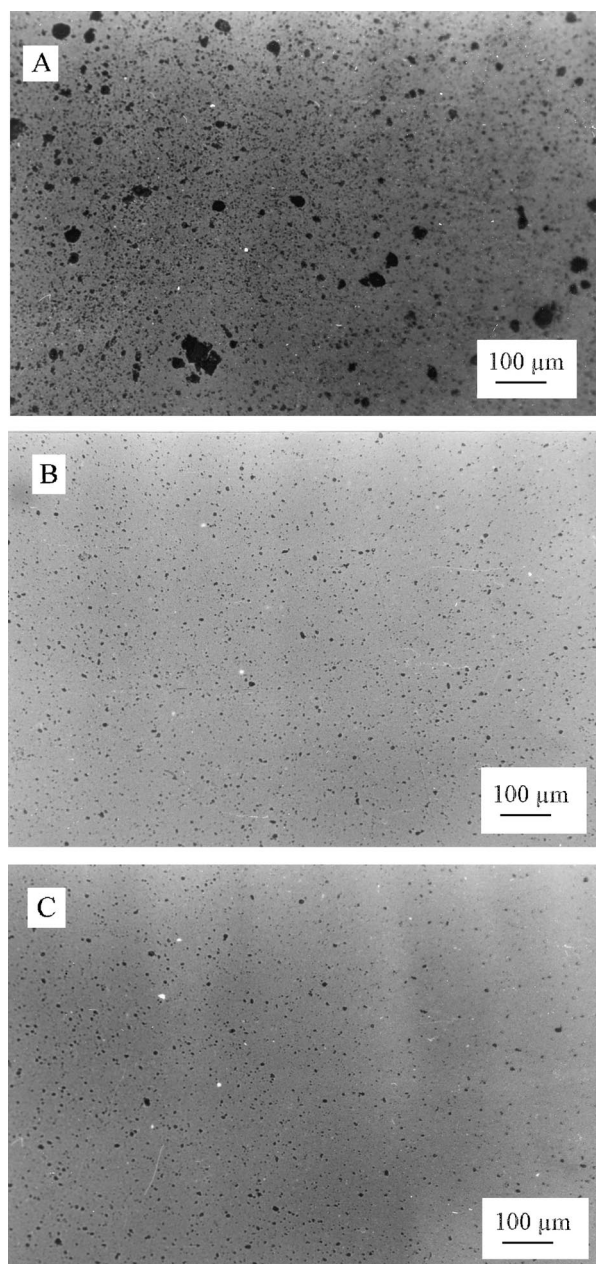


Fig. 4. Optical micrographs of slip cast SN2 samples prepared according to mixing routes (A) A, (B) B, and (C) C after sintering at 1750°C/1 h.

present, as a consequence of the high mechanical shearing. These bubbles could not be removed even after a further low speed agitation. This fact explains why route A was rejected for the obtention

of homogeneous, defect-free bodies. The same aspect is observed for the other compositions prepared by shear mixing. The aspect of sintered cast SN2 samples prepared by routes B and C can be seen in Fig. 4(b) and (c), respectively. As expected from the rheology and from the casting kinetics, route B allows the obtention of more uniform microstructures with smaller pore sizes for any composition. In samples prepared by route C occasional big pores can be also detected.

3.2 Pressure slip casting

Pressure slip casting experiments were performed for the three compositions after preparation of the slips by routes B and C, since route A was observed to give heterogeneous microstructures with remaining big pores.

The wall thickness formation rate is plotted in Figs 5 and 6 for the slips prepared by route B and C, respectively for an applied pressure of 6.8 MPa. The relative behaviour of the different compositions for each mixing route is similar, the casting rate being lower when sintering aids are introduced, similarly to the slip casting behaviour. It can be stated the strong difference in the kinetics of slip casting and pressure casting, in this case surpassing at least one order of magnitude. It can be observed once more, that pressure casting rate is higher for slips prepared by route C, as observed for slip casting, this being a consequence of the higher viscosity of the slips.

During pressure casting, an experimental problem is related to the fact that there is a certain time in which the piston has started the movement before the final pressure is achieved. When the final pressure is reached, filtering has started and a thin cake is already formed. The uncontrolled first step of casting can be the responsible for the differences found in the casting behaviour. If the values registered before reaching the final pressure are removed, the casting kinetics at constant pressure conditions are identical for the three compositions. This can be observed in Fig. 7, which represents the casting behaviour of the curves plotted in Fig. 5 considering only the part in which the pressure is

constant. The possible differences in the kinetics can be only associated to the first seconds of the process, in which the control is very limited. The pH of these suspensions was readjusted prior to casting, to avoid pH shifting, which modifies the rheology and then, the casting behaviour.

The green densities of the samples pressure cast at 6.8 MPa are shown in Table 3. Higher densities are obtained for mixing route B, as expected. However, the green densities are always lower than those obtained by slip casting, due to the much higher formation rate which difficults the arrangement of particles during forming.

The effects of the magnitude of the applied pressure on both the kinetics and the green microstructure of SN2 compositions was described in a previous work.¹³ The higher is the applied pressure the faster is the wall thickness formation rate. This statement is also valid during all the casting time, independently of the formation of the first cake when the final pressure is not yet reached. It can be noticed that when the applied pressure is higher the time required to reach the final pressure is lower, and for all the pressures it was observed that the formed first layer had the same thickness (1.8 mm).

The green density was very similar for any applied pressure (1.8 g cm⁻³).

From the casting kinetics at different pressures, the wall cast thickness can be represented as a

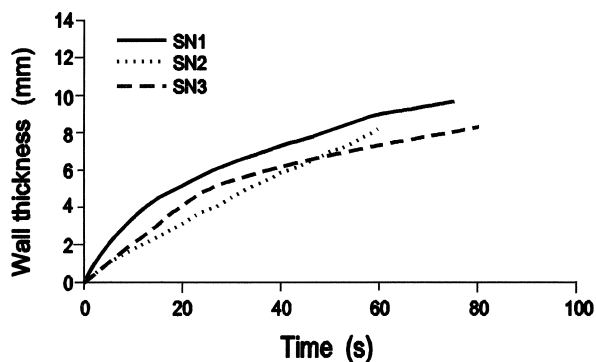


Fig. 5. Pressure casting kinetics of slips prepared by mixing route B.

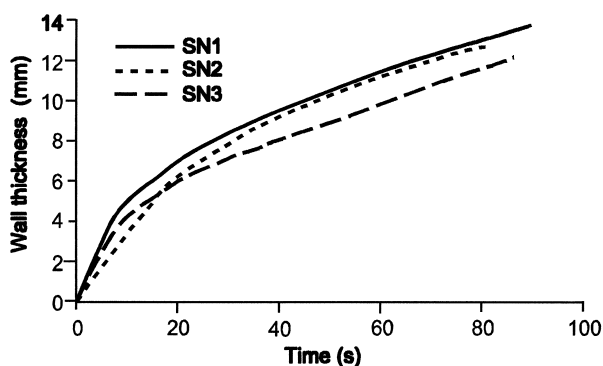


Fig. 6. Pressure casting kinetics of slips prepared by mixing route C.

function of the applied pressures for constant casting times, as plotted in Fig. 8. This plot is useful as a control in production cycles, where the feasibility of this manufacturing technique is limited by the effective pressure that can be applied with the available press.

All these experiments were made from the as-received powders. However, the as-received Y₂O₃ powder had a mean particle size of 3.5 μm, four times higher than that of the other components in the mixture, producing in some cases heterogeneities in the microstructure. Once the processing conditions facing the best rheological behaviour and the maximum casting control were established, pressure casting tests were also performed using a milled Y₂O₃ powder with a mean particle size of 0.8 μm. Figure 9 shows the evolution of cast thickness with time at the four considered applied pressures for SN2 slips prepared with the milled Y₂O₃. The casting curves are quite similar to those obtained using the as-received yttria powder,¹³ but it can be detected a small tendency to increase the casting rate when the milled powder is used. This is in good agreement with the small increase in viscosity reported in the rheological considerations. The corresponding green densities are shown in Table 4, where the densities obtained for pressure cast samples formed from the as-received powders are also included for comparison purposes. When milled yttria is used, the green density of the cast is inversely related to the applied pressure. A maximum relative density of 57.1% is obtained for 1.7 MPa, decreasing up to 55.0% for 10.2 MPa. This is the expected variation of density with pressure which

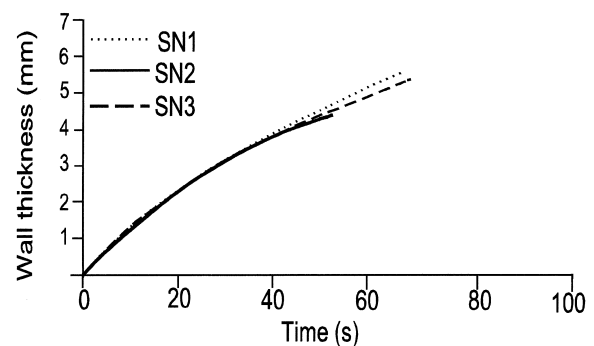


Fig. 7. Pressure casting kinetics of slips prepared by mixing route C from the point in which the maximum pressure is achieved.

Table 3. Green densities of pressure cast samples prepared by mixing routes B and C and pressed at 6.3 MPa

Mixing route	Density (g cm ⁻³)		
	SN1	SN2	SN3
B	1.67 ± 0.03	1.78 ± 0.03	1.77 ± 0.01
C	1.59 ± 0.03	1.66 ± 0.02	1.70 ± 0.02

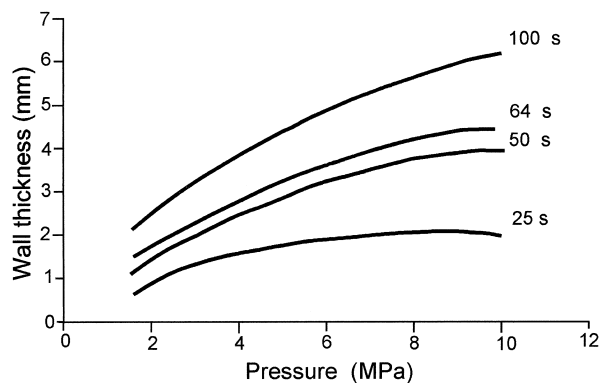


Fig. 8. Variation of the green body thickness with the applied pressure for different casting times of slip SN2.

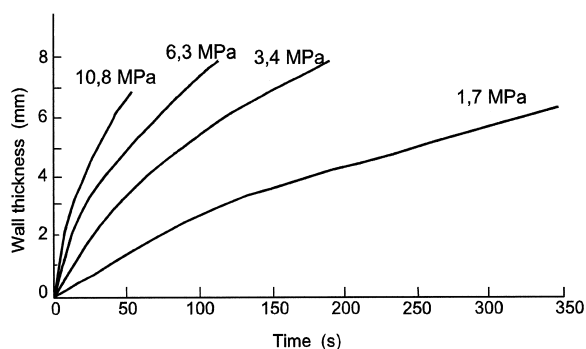


Fig. 9. Pressure casting kinetics of SN2 slips prepared by mixing route B from previously attrition milled yttria, at different applied pressures

contrasts with the abnormal independency found for the mixtures prepared from as-received yttria, where no clear tendencies could be stated. This is probably due to microstructural unhomogeneities promoted by the coarse, agglomerated starting yttria.

3.3 Surface characterization

In previous works^{14,15} it has been stated that the addition of TMAH as dispersant in aqueous silicon nitride slip inhibits a progressive surface oxidation because of the formation of a protective partially oxidized screen. Surface analysis were also performed by XPS for pressure cast green samples and the results compared with those obtained for slip casting.

The bending energy of core electrons determined by XPS for SN2 green compacts obtained by both colloidal filtration techniques (slip casting, SC, and pressure slip casting, PSC), as well as the corresponding surface atomic ratios are summarized in Table 5. The analysis were performed independently on the bulk of green samples and on the external surface in contact with the moulds.

In the case of slip casting, the presence of Ca^{2+} in the cast surface in contact with the plaster mould was already detected in previous experiments.¹⁵ This contamination evidences a major

Table 4. Green density of SN2 samples prepared by pressure casting at different pressures with as-received and with milled yttria

Casting pressure (MPa)	SN2		SN2-milled Y_2O_3	
	$\rho(\text{g cm}^{-3})$	$\rho(\% \text{ th})$	$\rho(\text{g cm}^{-3})$	$\rho(\% \text{ th})$
1.7	1.83 ± 0.03	56.3	1.86 ± 0.03	37.1
3.4	1.80 ± 0.03	55.4	1.82 ± 0.03	56.0
6.3	1.83 ± 0.03	56.3	1.80 ± 0.03	55.5
10.2	1.82 ± 0.03	56.0	1.79 ± 0.03	55.0

Table 5. Binding energy of core electrons and atomic ratios determined by XPS for slip cast (SC) and pressure cast (PSC) SN2 samples in the bulk and in the external surface

Sample	N1s	Si2p	N/Si	Al/Si	Y/Si
Bulk-SC	397.6 (89)	101.6 (65)	1.34	0.020	0.026
	398.6 (11)	102.3 (35)			
Surface-SC	397.3	101.7 (94)	0.929	0.299	0.094
		103.2 (6)			
Bulk-PSC	397.4 (86)	101.5 (83)	1.30	0.019	0.017
	398.4 (14)	102.7 (17)			
Surface-PSC	397.4 (90)	101.6 (82)	1.43	0.047	0.040
	398.5 (10)	101.7 (18)			

problem of slip casting as shaping technique, either in water or in nonaqueous solvents. However, this contamination is only detected in a thin layer of a few atoms and could be easily removed by simple machining. The XPS spectrum of this external surface reveals that Si2p peak has a very low concentration (6%) of oxidic particles (SiO_2) with a high binding energy value (103.2 eV). The N/Si atomic ratio is abnormally low and the O/Si ratio is very high, which demonstrates that the contact with the plaster mould not only produces calcium contamination but also promotes a extremely high surface oxidation. This is located as said before in a thin external layer and does not propagate to the bulk. On the other hand, the Al/Si and Y/Si atomic ratios are much higher than those registered in the bulk of the samples, thus indicating that there is a significative heterogeneity in the distribution of the oxidic sintering aids, whose concentrations increase markedly in the outer cast walls. This suggests that there is a migration or diffusion of these additives during forming, probably related to the particle flow during filtration process. On the other hand, the Al/Si and Y/Si ratios obtained for pressure cast bodies in the external surface duplicates the values registered in the bulk, suggesting also that some heterogeneity occurs, and those elements tend to migrate towards the external surface. Although this effect is very much reduced with respect to slip cast bodies, it must be related not only to interactions with the mould but also to the heterogeneity in the particle size.

Table 6. Binding energy and atomic ratios determined by XPS for slip cast (SC) SN2 samples prepared with milled Y_2O_3 ; in the bulk and in the external surface

Sample zone	N1s	Si2p	N/Si	Al/Si	Y/Si
Bulk	397.5 (90)	101.6 (86)	1.30	0.021	0.019
	398.6 (86)	102.7 (14)			
Surface	397.5 (92)	101.6 (87)	1.448	0.032	0.028
	398.5 (8)	102.7 (13)			

In order to clarify this point, XPS analysis were also performed for slip cast green samples prepared using the milled yttria. In this case, analysis were made also on the bulk of the samples and in the external surface in contact with the mould. The bending energy of the N1s and Si2p peaks and the corresponding atomic ratios are shown in Table 6. The most important differences here are the Al/Si and Y/Si ratios, which are around 0.020 in the bulk of the samples and increases up to around 0.030 in the external surface. This increased ratio is lower than in the case of pressure casting, whose atomic ratios increase from around 0.018 in the bulk to more than 0.040 in the surface, and very much lower than in the slip casting performed with the as-received yttria.

The characterization of the green samples by XPS allows the prediction of the uniformity of the additives distribution in the sintered material. The other processing parameters, such as powder characterization, rheological behaviour, casting kinetics, etc., did not give this kind of information. This point will be discussed below in the light of microstructural observations in the sintered compacts.

Summarizing the results of the surface analysis, it can be stated that slip casting provides a significant contamination to the external walls of the body. The major advantage of pressure casting is usually related to the increased casting rates facing an improved productivity. But a second and also important advantage is that it could be designed the system in such a way that the cast is not contaminated by the mould and then the impurities and the local oxidation at the external surfaces are strongly reduced. In addition, this promotes a more homogeneous distribution of the sintering aids.

3.4 Sintering experiments

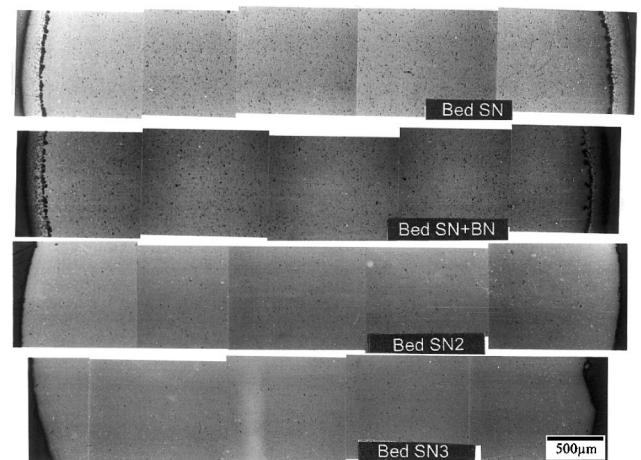
The spontaneous tendency to decomposition seriously difficults the pressureless sintering of silicon nitride parts. Many different parameters influence the characteristics of the fired compact. Between them, the sintering temperature and soaking time, the heating and cooling rates, the N_2 flowing pressure in the furnace chamber, the possibility of applying vacuum in the first steps and the nature of the sintering bed, have been proven to be

determining parameters in the final results. In this work, all these parameters were taken into account by testing at different conditions slip cast samples with composition SN2. According to these previous studies the sintering temperature and time were fixed at $1750^\circ C/1-2 h^{-1}$, with a heating rate of $10-20^\circ C min^{-1}$, using an overpressure of N_2 of 20 kPa and applying vacuum up to $750^\circ C$ in order to promote O_2 elimination.

The most significant differences were found in relation with the sintering bed employed for the tests. Four sintering beds were considered: (1) Si_3N_4 powder; (2) Si_3N_4 powder after coating the sample with spray of BN; (3) a previously homogenized mixture of Si_3N_4 with Al_2O_3 and Y_2O_3 in the same proportions that in the sample to be sintered (SN2 composition); and (4) a bed composed by a mixture of SN3 composition, that is, with a concentration of oxides higher that the sample SN2 to be sintered. The final densities and the weight loss obtained at the same conditions as a function of the sintering bed are shown in Table 7. A general view of the sintered materials can be seen in the micrographs of Fig. 10. When Si_3N_4 powder is used as sintering bed, the final density is low and the weight loss is large. In the corresponding micrograph (Fig. 10) the presence of a porous layer near the edge sample is clearly observed. This is a consequence of the volatilization of Si_3N_4 . When

Table 7. Density of sintered compacts obtained by slip casting using the different mixing routes

Sample	Mixing route A	Mixing route B	Mixing route C
SN2	3.09 ± 0.01	3.18 ± 0.03	3.11 ± 0.02
SN2-milled Y_2O_3	3.08 ± 0.02	3.24 ± 0.02	3.26 ± 0.02
SN3	3.13 ± 0.03	3.15 ± 0.01	3.16 ± 0.03

**Fig. 10.** General picture showing the influence of the sintering bed on the external surfaces of samples SN2 sintered at $1750^\circ C/2h$.

sintering was performed with samples coated by BN higher densities are obtained but the weight loss is also high. In the microstructure of this sample [Fig. 10(b)] the porous layer near the surface is also clearly observed. This could be related to the different shrinkage behaviour allowing the compact surface to be directly exposed to the Si_3N_4 bed during cooling, and the same aspect is seen in the picture. When the bed has the same composition of the sample the density increases and the weight loss is reduced because the atmosphere around the sample is the same that into the sample, thus reducing diffusion and volatilization phenomena. In this case a more homogeneous microstructure is obtained without the porous external layer [Fig. 10(c)]. In the case of a bed of SN3 composition [Fig. 10(d)] the picture is similar but the density is reduced. The problem in this case is the strong interaction between the sample and the bed.

Independently of the sintering bed, the presence of bright precipitates near the external surfaces is observed in all cases. This is probably originated as a consequence of local changes in the liquid phase composition during sintering. This effect is not only observed in slip cast samples but also in pressure cast ones, as can be observed in Fig. 11, where

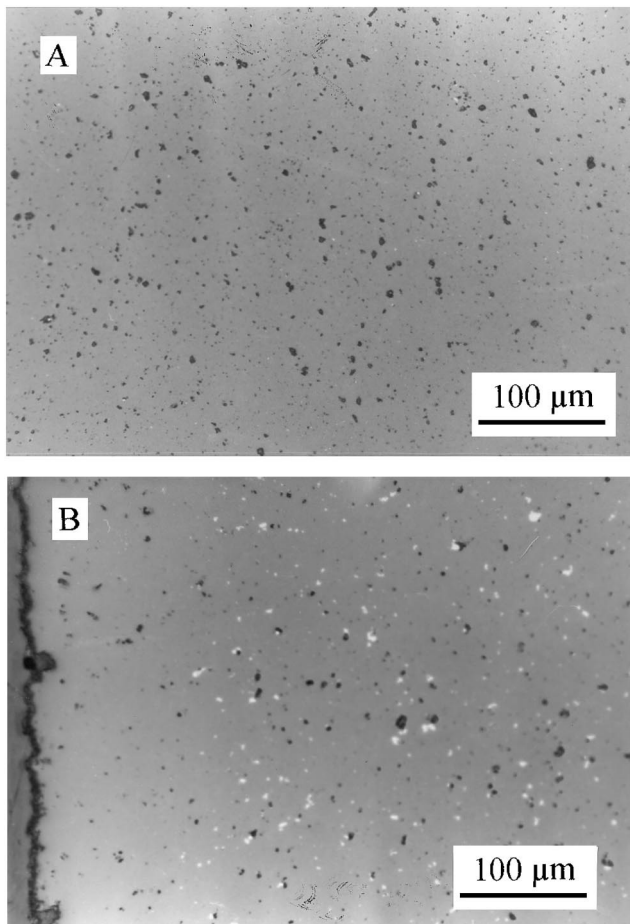


Fig. 11. Microstructure of (A) the centre and (B) the edge of a pressure cast, sintered SN2 sample (using the as-received yttria).

the microstructures of bulk and edge areas of pressure cast SN2 samples are shown. Consequently it cannot be related to contamination promoted by plaster moulds. When milled yttria is employed a more homogeneous microstructure is obtained and these precipitates are still present but at lower concentrations. Figure 12 shows the microstructure of the edge of a sintered SN2 slip cast specimen prepared with milled yttria. These results are in good agreement with the previously reported surface analysis, where the heterogeneous distribution of the sintering aids was detected before sintering.

The final densities of the sintered slip cast compacts obtained for SN2 and SN3 compositions with the as-received sintering aids and for SN2 prepared with milled yttria are shown in Table 7. The values are in line with all previous processing steps. Mixing procedure B gave lower viscosities and lower casting rates and hence, the final densities are higher. The final value is enhanced when yttria is previously milled, as expected from the XPS and microstructural analysis. In the case of pressure casting the final densities are lower than in slip casting, as shown in Table 8, but no significant differences in density were found for the different

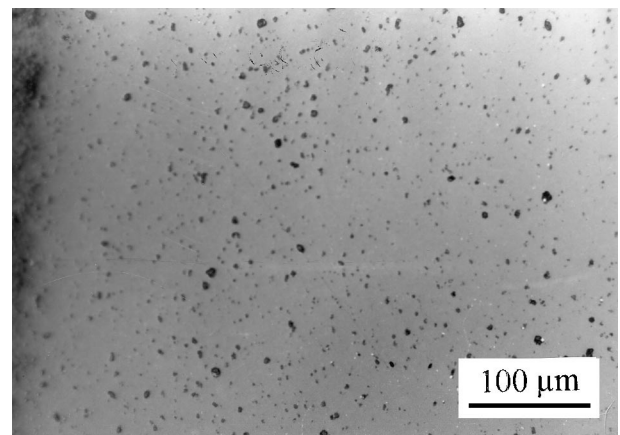


Fig. 12. Optical micrograph of the edge of a slip cast SN2 sample prepared with milled yttria.

Table 8. Density, shrinkage and weight loss of sintered compacts obtained by pressure casting using different pressures

Sample	Pressure (MPa)	Density (g cm^{-3})	Linear shrinkage (%)	Weight loss (%)
SN2	1.7	3.14 ± 0.02	—	—
	3.4	3.18 ± 0.01	14.19	2.10
	6.3	3.17 ± 0.01	16.43	2.21
	10.2	3.16 ± 0.02	18.20	1.84
SN2-milled Y_2O_3	1.7	3.11 ± 0.03	18.79	3.39
	3.4	3.10 ± 0.02	18.94	3.38
	6.3	3.12 ± 0.01	19.70	3.73
	10.2	3.13 ± 0.02	21.52	3.38

applied pressures. On the other hand, and oppositely to that found for slip casting, the use of milled yttria produces a decrease in the sintered densities.

Another problem of silicon nitride materials is their preparation for SEM observations. In this work chemical etching was performed at 275°C using an alkaline mixture. The best grains definition was achieved after 25–30 min etching. Figure 13 shows the microstructures obtained by SEM on sintered and etched surfaces for slip cast [Fig. 13(a)] and pressure cast [Fig. 13(b)] SN2 compacts. Some agglomerates can be detected, specially in the case of pressure casting. The homogeneity is improved using milled yttria, as can be observed in the SEM micrographs of Fig. 14, corresponding to slip cast [Fig. 14(a)] and pressure cast [Fig. 14(b)] specimens.

After chemical etching liquid phases located at grain boundaries are eliminated. The silicon nitride crystals present a bimodal microstructure with a major presence of rod-like grains, typical of β -Si₃N₄,

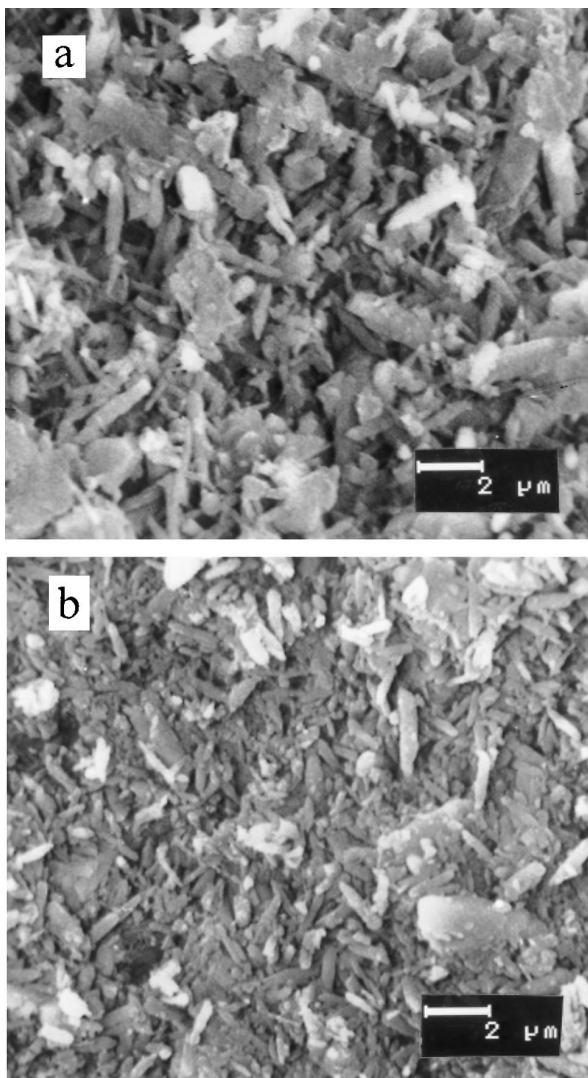


Fig. 13. SEM micrographs of (a) slip cast and (b) pressure cast SN2 samples sintered at 1750°C/2h.

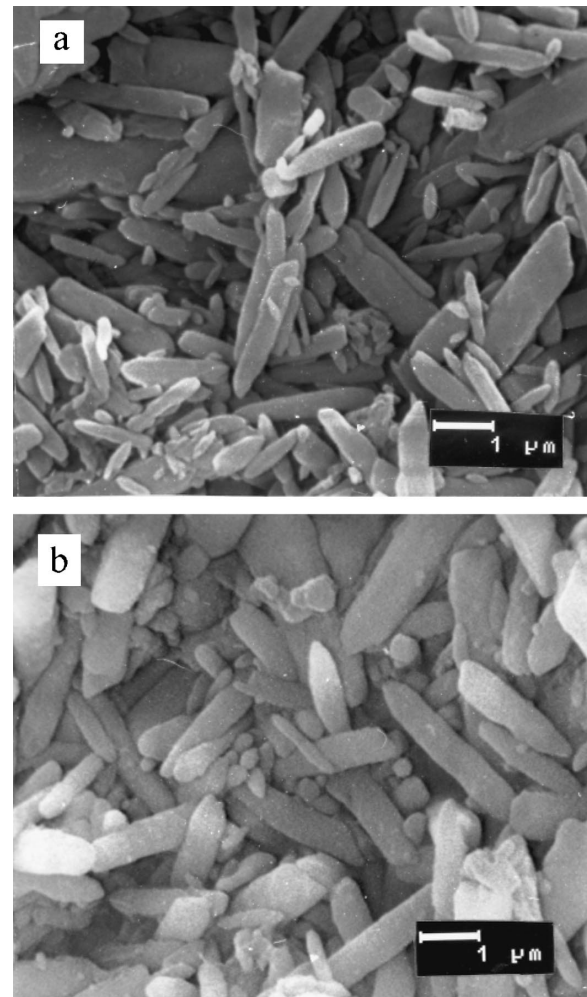


Fig. 14. SEM micrographs of (a) slip cast and (b) pressure cast SN2 samples sintered at 1750°C/2h, obtained using the milled yttria powder.

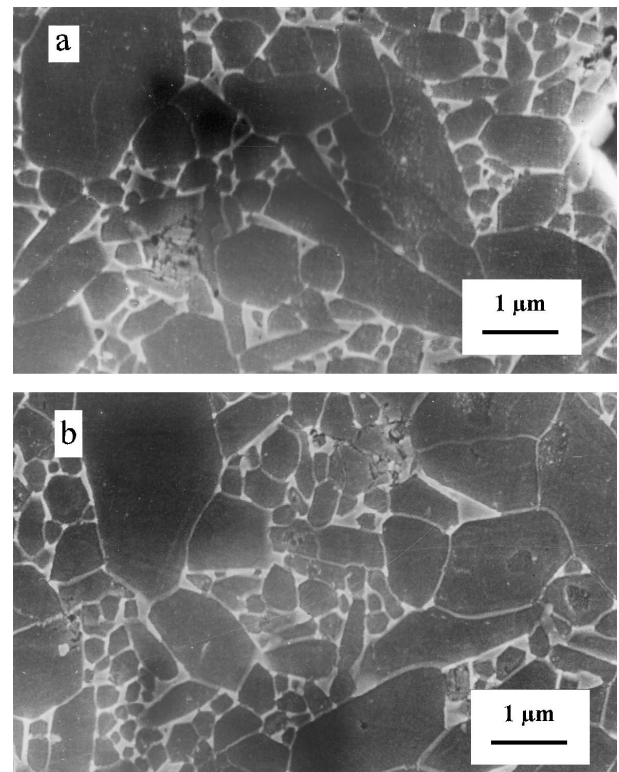


Fig. 15. SEM micrographs of (a) slip cast and (b) pressure cast SN2 samples sintered at 1750°C/2h, after plasma etching.

Table 9. Hardness and toughness of sintered slip cast compacts

Composition	H_v (GPa)	K_{IC} (MPa $m^{1/2}$)
SN2	12.8 ± 0.3	6.4 ± 0.1
SN2-milled Y ₂ O ₃	12.2 ± 0.3	6.2 ± 0.1
SN3	12.6 ± 0.3	6.2 ± 0.3
SN3-milled Y ₂ O ₃	14.1 ± 0.3	6.6 ± 0.1

Table 10. Hardness and toughness of sintered pressure cast compacts

Composition	SN2		SN2-milled Y ₂ O ₃	
	H_v (GPa)	K_{IC} (MPa $m^{1/2}$)	H_v (GPa)	K_{IC} (MPa $m^{1/2}$)
Pressure (MPa)				
1.7	12.4 ± 0.3	6.2 ± 0.2	12.4 ± 0.2	5.9 ± 0.3
3.4	13.6 ± 0.5	6.4 ± 0.1	13.0 ± 0.7	6.3 ± 0.1
5.4	12.9 ± 0.5	6.3 ± 0.1	—	—
6.3	—	—	13.0 ± 0.2	6.7 ± 0.1
10.2	13.3 ± 0.4	5.8 ± 0.4	13.9 ± 0.7	6.2 ± 0.1

as it was identified by X-ray diffraction. The intergranular phases can be better visualized in Fig. 15(a) and (b), where the microstructure of slip cast and pressure cast samples treated by plasma etching with CF₄ are observed.

In order to evaluate the properties of the obtained sintered materials, room temperature Young's modulus and toughness were determined, as summarized in Tables 9 and 10. These properties were determined by microindentation tests for an applied load of 50 kg. The ratio between the crack length (c) and the indenter diameter (a) was $c/a > 2.5$, as desired for indentation tests. Taking into account that the studied compositions were selected for adjusting the processing parameters the obtained values are high enough and can be compared with the obtained by other authors by pressure sintering. On the other hand, no significant differences are found between the different forming processes, and between the different applied pressures in pressure casting. However, there are differences as demonstrated by surface and microscopical analysis. These differences are not detected in the E and H room temperature values, but probably these properties are affected at higher temperatures by processing conditions.

4 Summary

In this series of works all the processing steps for the obtention of pressureless sintered silicon nitride parts by colloidal filtration techniques have been studied, relating any processing step with previous and next processing steps. As demonstrated along the paper the best rheological prop-

erties are obtained for prolonged low energetical mixing of 65 wt% solid loadings at pH = 11.5 in a ball mill (24 h), which produce lower casting rates and subsequently, higher green densities (near 60% th). Surface analysis by XPS and microstructural observations confirmed all the processing parameters. Slip casting moulds produce a significant Ca contamination and promotes a noticeable surface oxidation in a thin external layer. The use of fine grained sintering aids tend to reduce this effect but it does not completely disappear. On the other hand, pressure casting kinetics is 20 times faster than slip casting one, then allowing the process scale-up to industrial productions. The decrease in the green density can be neglected when considering the technological improvements of the technique for a continuous production. Furthermore, the use of pressure cast avoids the contamination derived from the plaster moulds and the subsequent surface oxidation degree.

Finally, the controlled slip processing studied in this work allows the obtention of pressureless sintered silicon nitride with relative densities higher than 96% th, and good values of hardness and toughness are measured, very near to those reported for pressure sintered parts.

Obviously, the starting compositions were not selected facing the improvement of any particular property, but the controlled sequency of processing steps stated along the paper allow us to design and prepare any composition of this system searching the enhancement of a determined property.

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