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Aqueous injection moulding of silicon nitride

A.J. Millán [1], M.I. Nieto, R. Moreno *

Instituto de Cerámica y Vidrio, CSIC, 28500 Arganda del Rey, Madrid, Spain

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Abstract

The fabrication of pressureless sintered silicon nitride parts by low pressure injection moulding of aqueous slurries is described. A basic requirement for this process is the preparation of a stable suspension with high solids content and appropriate rheological properties. The temperature has also a determining role in the stability conditions of the slip. In this work the effect of temperature on the rheological behaviour of silicon nitride aqueous slips was studied taking into account slip parameters such as the type and concentration of deflocculant, pH, ageing, etc. Once the stability conditions were determined, the effect of a gelling agent (agarose) on the slip rheology was also studied in order to optimize the injection conditions. The rheological behaviour of slips containing 1 wt.% agarose was studied as a function of temperature as well as the influence of sintering aids. Injection moulding was performed at temperatures of 60–65°C and a pressure of 0.4 MPa. Final densities of about 90% theoretical are obtained after sintering at 1750°C in N_2 flow. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Forming; Injection moulding; Rheology; Si_3N_4

1. Introduction

The application of colloidal science to ceramic manufacture has proved to provide more homogeneous materials with controlled microstructure and increased reliability.[1,2] An additional advantage of colloidal forming is the possibility to obtain complex-shaped parts.

Ceramic injection moulding is a well-established shaping technique, which involves the mixing of ceramic powder with a large concentration of a melt polymer (up to 50 vol.%).[3,4] The carrier polymer provides very high viscosity, so very high pressures (10–150 MPa) and temperatures (120–200°C) are needed for injection. In addition to the high cost derived from the use of organics the major problem arises from the debinding step which can easily lead to defects and failure of the sintered body.[5]

Aqueous injection moulding strongly reduces the binder requirements and provides an environmentally friendly technology as the solvents and polymers are substituted by water and low concentrations (2–3 vol.%) of non-contaminant additives like those used in the food industry.[6–8] This makes possible the preparation of a conventional aqueous suspension to which a gelling additive is added. The low viscosity of these suspensions allows an accurate control of the colloidal chemistry which helps to reduce defects size and number and improves reproducibility. Besides, gelling additives provide a much higher green strength, so green ceramic parts are easily handled and machined.

Among the additives that form a consistent gel by cooling a warm ceramic suspension the most efficient is the agarose.[8–11] A solution in water containing 2 wt.% agarose provides a gel strength higher than 1200 g/cm^2.[12] The slip is prepared conventionally like in the case of slip casting or pressure casting. After preparing a well-dispersed suspension of the ceramic powder, the gelling agent is added and mixed. This mixing step requires the slip to be heated at 60–70°C. This method has the potential advantages of colloidal processing and provides very strong green bodies. Other additives such as agar,[12,13] starches[14] and gelatin[15] are being investigated. The research in this field is starting and trying to offer a variety of additives with good gelling properties at a low cost. This technology has been mostly applied for manufacturing alumina ceramics. Although the dispersability of alumina in water is widely reported, the

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* Corresponding author. Tel.: +34-9-1871-1800; fax: +34-9-1870-0550.

[1] Permanent address: Departamento Materiales, IUT Dr. Federico Rivero Palacios, Caracas, Venezuela.

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temperature requirements of the injection slip need a careful control of the rheology in those conditions.[16,17] The new approach is to follow the gelling process in such a way that viscosity can be maintained low but a strong gel can be obtained when cooling below the glass transition temperature.

The success reached for alumina ceramics encourages the application of this attractive shaping technology to non-oxide ceramics such as silicon nitride. Previous works have established the preparation conditions of well-dispersed silicon nitride aqueous slips for colloidal filtration processes.[18] Low viscosity slips can be prepared by adjusting pH at 11–11.5 with tetramethylammonium hydroxide (TMAH). However, the effect of temperature on the dispersing state of these slips has not been yet reported in the literature.

The aim of this work is to investigate the rheological behaviour of aqueous silicon nitride slips as a function of pH and temperature and to establish a procedure for obtaining of silicon nitride parts by LPIM in water using agarose as gelling agent.

2. Experimental

A commercial silicon nitride powder (Hermann C. Starck LC12N, Germany), with a mean particle size of 0.7 μm and a specific surface area of 18 m^2/g was used. Pressureless sintering by means of a liquid phase requires sintering aids. For such purpose, alumina and yttria were used in concentrations of 3 wt.% each. The Al_2O_3 powder (Condea HPA05, USA) had a mean particle size of 0.4 μm and a surface area of 9.5 m^2/g. The as-received Y_2O_3 powder (Mandoval, UK) had a mean particle size of 3.5 μm, but it was attrition milled down to a mean diameter of 0.8 μm, as reported in Ref. 18.

Aqueous slips of silicon nitride were prepared at high pH values by adding tetramethyl and tetrapropyl ammonium hydroxides (TMAH and TPAH, Aldrich Chemie, Germany) as deflocculants. These are supplied as solutions in water with concentrations of 25 wt.% and 1 M, respectively.

The slips were prepared to solid loadings of 70 wt.% (42.9 vol.%) by ball milling 24 h in a plastic bottle with nylon balls. Rheological studies were carried out for each dispersant at different pH conditions and temperatures ranging from 25 to 70°C. The ageing behaviour of all the slips was studied by measuring the rheological properties of the fresh slips and after 24 and 48 h. For ageing tests the slips were maintained under rotation in a closed vessel.

After determining the best dispersing conditions for silicon nitride, the sintering aids were incorporated to the slip and homogenised by 4 h ball milling. The slips containing the sintering aids (41.8 vol.%) were also characterised.

The rheological characterisation was performed using a rheometer (Haake, rheostress RS50, Germany) operating at controlled rate with double cone and plate geometry. The conductivity of all prepared slips was measured with a conductivity meter (LF320, WTW, Germany).

Once the dispersing conditions of the silicon nitride slips as a function of temperature were studied the gelling agent was added. An agarose (Hispanagar D1-LE, Spain) was used as binder. The characteristics of this additive were studied before.[17] In this work, a concentration of 1 wt.% (referred to solids) of the powdered binder was added on the well-dispersed slip containing also the sintering aids. Homogenisation of the binder was performed by 2 h ball milling to obtain the injection slip whose rheological behaviour was studied as a function of temperature.

Injection tests were performed in a manual LPIM machine (Peltsmann MIGL28, USA) controlling the temperature in the tank and in the orifice between 55 and 65°C, for residence times into the mould cavity of 2–30 s. A pressure of 0.4 MPa was applied. A steel mould cooled by flowing water was used to produce test bars with 60×10×10 mm. The as-injected bars were left in air 24 h for drying. Green densities were measured by mercury immersion. Linear shrinkage was measured after drying. Sintering was performed at 1750°C/2 h under N_2 flow in a graphite chamber furnace (Astro, Thermal Technology, USA). The green and the sintered microstructures were evaluated by scanning electron microscopy on fracture surfaces.

3. Results and discussion

Aqueous slips were prepared to solids contents of 70 wt.% (42.9 vol.%, when no sintering aids are present) at different pHs using both hydroxides. Fig. 1 shows the viscosity of the slips as a function of pH at a shear rate of 100 s^{-1}. This rate corresponds to the estimated shear operating on the slip during injection.[17] It can be

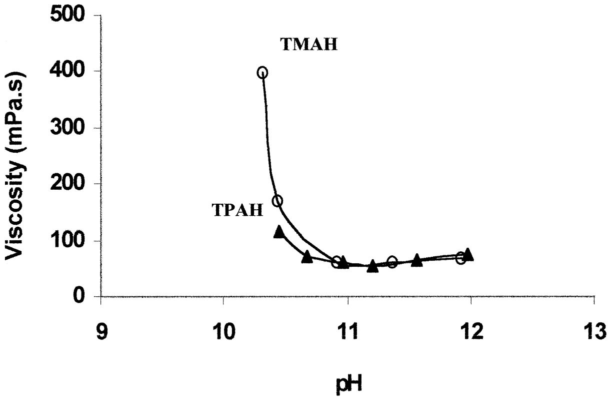

Fig. 1. Viscosity vs pH of the 70 wt.% slips for both dispersants at a shear rate of 100 s^{-1}.

observed that viscosity is very low above pH 11.0 in both cases, but at 10.5 the viscosity of the slip dispersed with TMAH strongly increases. In all cases the slip is dilatant when pH < 11 thus restricting the working pH to higher values where plastic or pseudoplastic behaviour is obtained. This behaviour is preferred in forming operations to avoid segregation during consolidation and drying. The small differences in viscosity below pH 11 could be related to a higher efficiency of the larger molecule (TPAH).[19] However, when the pH is high enough both dispersants provide a similar very low viscosity because of the strong repulsive electrostatic potential.

Another parameter affecting reliability of the LPIM process is the possible influence of slip ageing. The rheological behaviour of the slips was studied on the fresh slips but also after ageing for 24 and 48 h. The flow curves of fresh and aged 70 wt.% slips at pH 11 with TPAH and TMAH are shown in Figs. 2 and 3, respectively. Storage time makes the pH to slightly decrease and consequently viscosity increases. After 48 h ageing, the slip tends to become dilatant as a consequence of that change in pH.

The evolution of the rheological behaviour with temperature of these slips was studied. Figs. 4 and 5 show the variation of viscosity with temperature for fresh and aged slips dispersed with TPAH and TMAH respectively. A summary of the viscosity values is reported in Table 1. The viscosity tends to decrease below 60°C due to the corresponding decrease in water viscosity, but for higher temperatures a strong increase is observed indicating that dispersing efficiency is decreasing. On the other hand, ageing has a significant influence on the rheology of these slips. When the slips are aged at room temperature for 24 and 48 h the viscosity increases. This increment is negligible for TMAH but significant for TPAH. These differences increase with temperature, especially in the case of using TPAH. Consequently, considering the temperatures employed for LPIM, TMAH is recommended.

The pH of the slips decreases in 0.5 units as temperature increases between 25 and 65°C. This change in pH can suggest a loss of stability so that further additions of dispersant should be necessary. However, it has been observed that the change in pH is quasi-reversible with

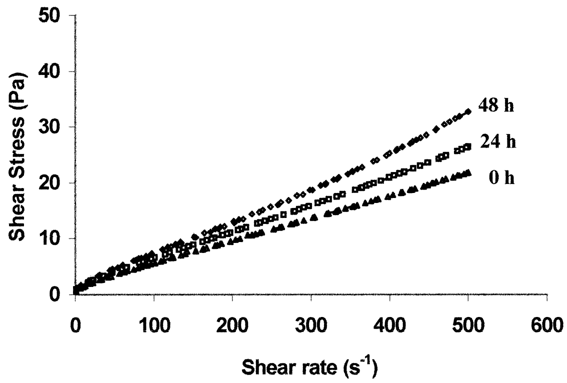

Fig. 2. Flow curves of fresh and aged 70 wt.% silicon nitride slips prepared at pH = 11 with TPAH.

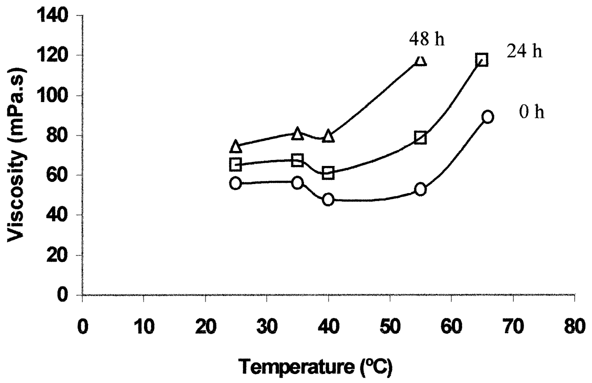

Fig. 4. Evolution of viscosity with temperature for fresh and aged 70 wt.% silicon nitride slips dispersed with TPAH.

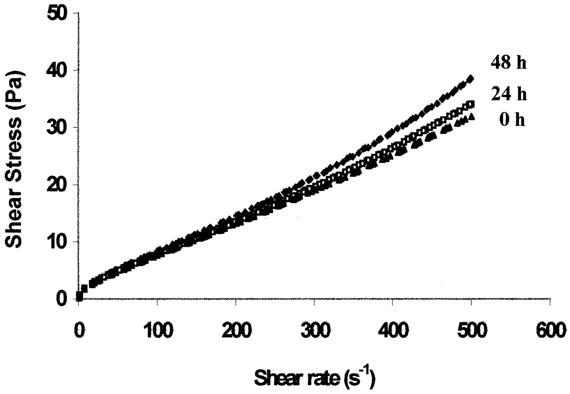

Fig. 3. Flow curves of fresh and aged 70 wt.% silicon nitride slips prepared at pH = 11 with TMAH.

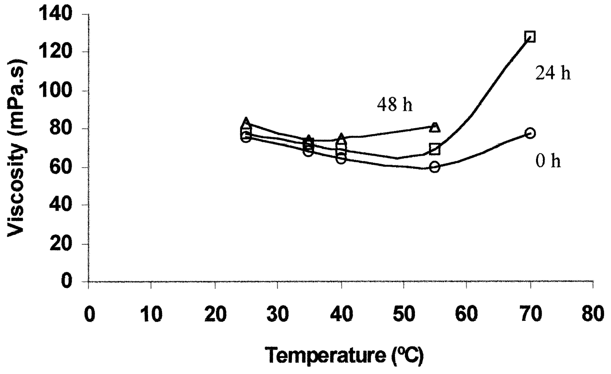

Fig. 5. Evolution of viscosity with temperature for fresh and aged 70 wt.% silicon nitride slips dispersed with TMAH.

temperature as well as the change in conductivity, as shown in Fig. 6 for a slip dispersed with TPAH. This suggests that no loss of dispersant by evaporation is occurring, as initially suspected. Hence, the viscosity increase is related to a tendency of particles to aggregate because of the changing properties of the solvent with temperature.

For the injection of sinterable parts of silicon nitride, the effect of sintering aids in the rheological behaviour was studied. Concentrations of 3 wt.% Al_2O_3 and 3 wt.% Y_2O_3 (referred to total solids) were added to the silicon nitride.[18] Slips were prepared to a total loading of 70 wt.% solids, this giving a volume percentage of 41.8. The flow curves of the slips with sintering aids at different temperatures are plotted in Figs. 7 and 8, corresponding to dispersion with TPAH and TMAH, respectively. As in the case of pure silicon nitride slips the viscosity first decreases when temperature increases and above 55°C increases. The viscosities are very similar for both dispersants and a Bingham plastic flow with a low yield point is obtained for any temperature. The small differences with respect to the pure silicon nitride slips are more related to the change in the volume concentration of particles than to a proper effect of the sintering aids.

The effect of gelling agent on the rheological behaviour was studied for slips prepared with both dispersants also. The flow curves at different temperatures are plotted in Figs. 9 and 10. The viscosity is lower for TPAH at low temperatures, but for injection temperatures TMAH gives lower viscosities, confirming that it is more suitable for LPIM. The addition of 1 wt.% agarose produces an important increase of viscosity (from 74 to 485 mPa s at 100 s^{-1} and 65°C after agarose addition). This strong increase of viscosity above 60°C is due to the fact that the binder should dissolve on heating.

For comparison purposes, Fig. 11 shows the variation of viscosity with temperature of the pure Si_3N_4 slip, the slip containing sintering aids and the injection slip, including also the gelling binder. In all cases TMAH was used as dispersant to a $pH > 11$. After agarose dissolution at 65°C the slip was injected at temperatures of 55, 60

Table 1
Viscosity values (mPa s) of 70 wt.% slips for both dispersants at $\dot{\gamma} = 100\ s^{-1}$, at different temperatures and ageing times ($pH > 11$)

T (°C)	Ageing time (h)	Viscosity (mPa s)	
		TPAH	TMAH
25	0	56	76
	24	65	78
	48	75	83
55	0	53	60
	24	79	69
	48	118	81
70	0	89	78
	24	118	128
	48	Uncontrolled	Uncontrolled

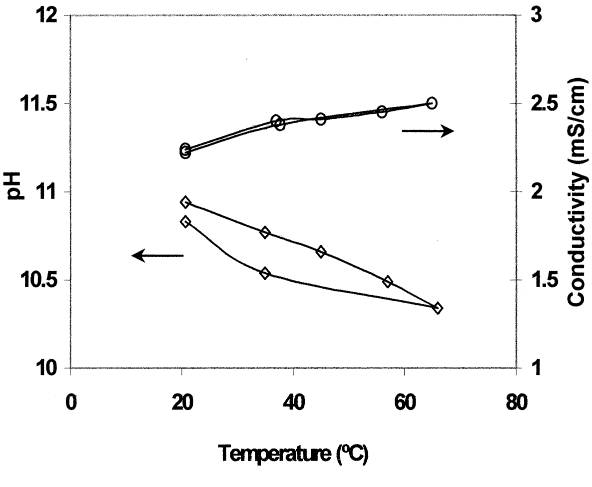

Fig. 6. Evolution of pH and conductivity with temperature for silicon nitride slips dispersed with TPAH.

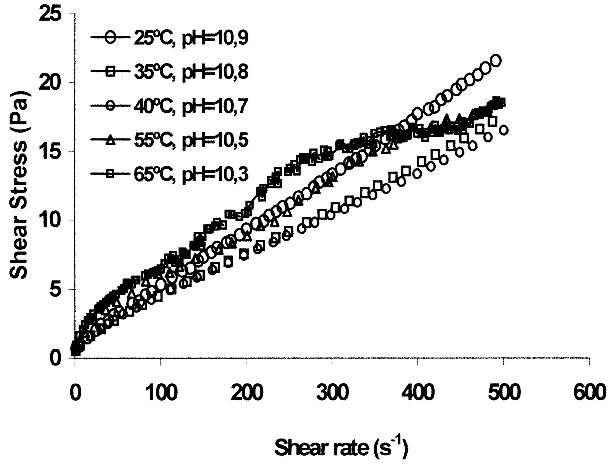

Fig. 7. Flow curves of slips with sintering aids at diferent temperatures dispersed with TPAH.

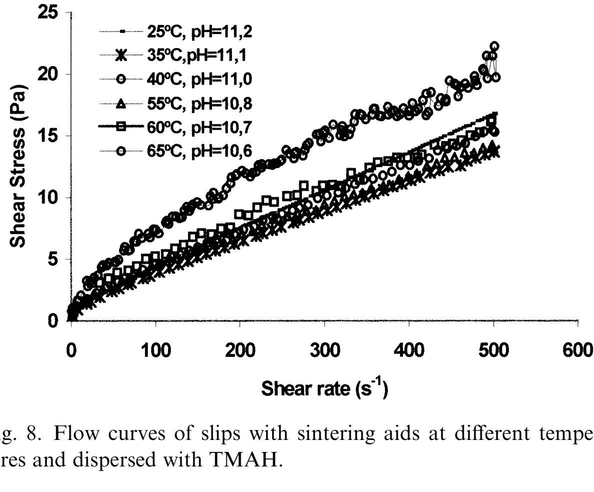

Fig. 8. Flow curves of slips with sintering aids at different temperatures and dispersed with TMAH.

and 65°C applying a pressure of 0.4 MPa. Injected test bars were left to dry in air. The values of green density and linear shrinkage of the samples are reported in Table 2. No influence of the tank temperature on the properties of injected parts was observed in the considered range. In addition, pressure and residence time are irrelevant parameters if a complete filling of the mould is assured.

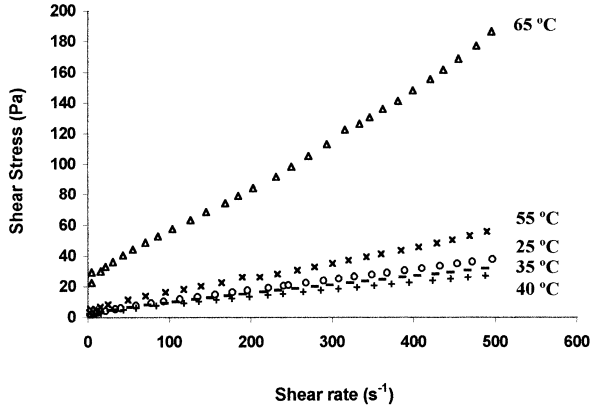

Fig. 9. Flow curves of slips with sintering aids and gelling agent at different temperatures dispersed with TPAH.

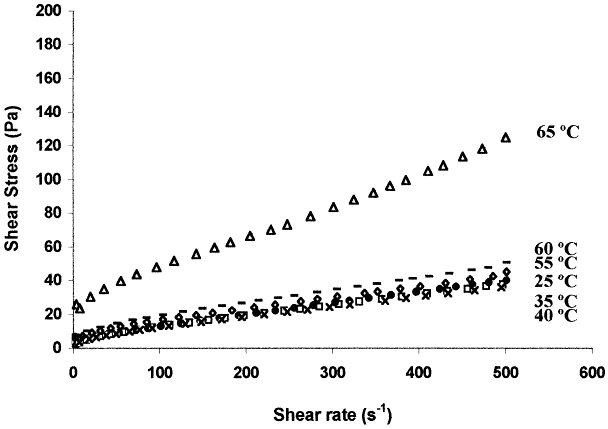

Fig. 10. Flow curves of slips with sintering aids and gelling agent at different temperatures dispersed with TMAH.

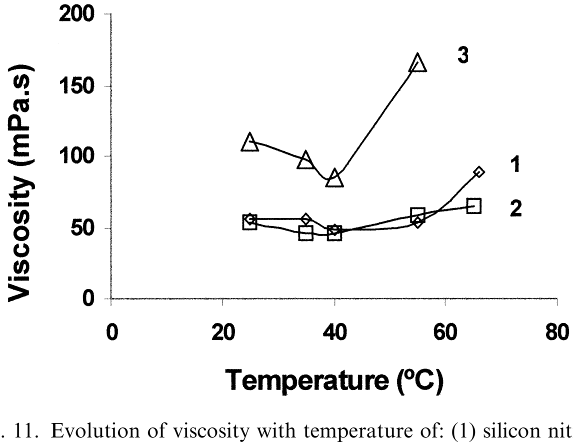

Fig. 11. Evolution of viscosity with temperature of: (1) silicon nitride slip, (2) silicon nitride slip with sintering aids and (3) silicon nitride slip with sintering aids and gelling agent.

Once the agarose has been incorporated its viscosity remains almost unchanged when decreasing temperature in a broad margin, up to near the gelling temperature, T_g. This shows the high viability of the process, which is not clearly dependent on critical processing conditions, excepting the T_g of the additive and a proper mixing so to reach an homogeneous mixture.

Fig. 12 shows a SEM micrograph of a fracture surface of a green sample. A good homogeneity and a small grain size can be appreciated. After sintering at 1750°C/2 h in N_2, the microstructure reveals a high uniformity without large deffects, as can be observed in the fracture surface microstructure shown in Fig. 13. The final density of the injected parts is around 90% theoretical, lower than the obtained by slip casting, as a consequence of the lower green density.

Optimisation to high densities requires the improvement of the gelling addition by dissolving it at higher temperatures. Although further improvements are necessary, a first approach has been made, proving the capability of the LPIM process for the near net shaping of pressureless sintered silicon nitride parts.

Table 2
Relative green density (RD) and linear shrinkage (ΔL) values of green samples injected at different temperatures

Tank temperature (°C)	RD (%th)	ΔL (%)
65	50.5±0.4	4.4±0.4
60	50.7±0.3	4.2±0.3
55	50.4±0.4	4.3±0.4

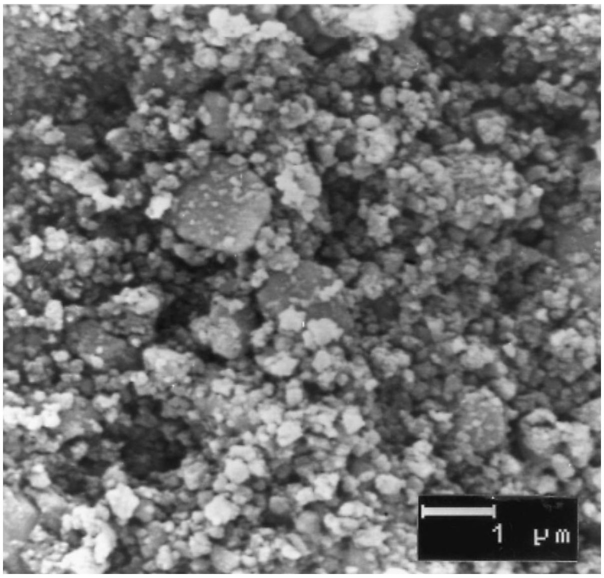

Fig. 12. Fracture micrograph of a green silicon nitride body obtained by SEM.

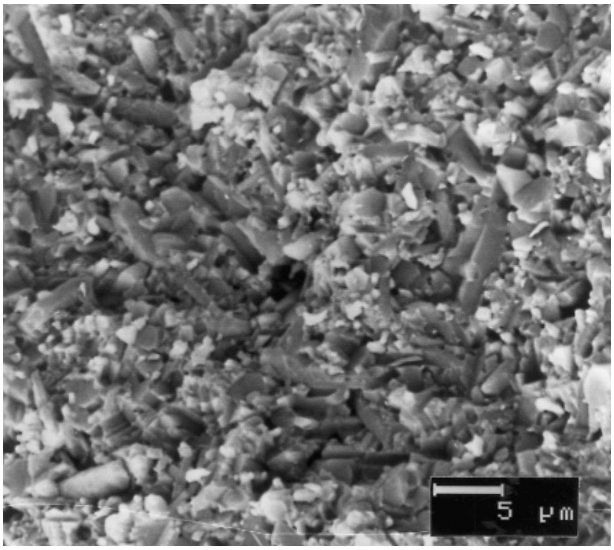

Fig. 13. Fracture micrograph of a sintered silicon nitride body obtained by SEM.

4. Conclusions

Concentrated aqueous silicon nitride slips (>40% vol) can be stabilized at pH 11–11.5 with strong bases, as TMAH and TPAH. The temperature has a significant influence on the slip rheology, especially above 65°C. When increasing temperature, the pH slightly decreases, but this change is reversible and it tends to recuperate on cooling.

Sintering aids (total concentration, 6 wt.%) do not influence the rheological behaviour of the silicon nitride slip neither at room nor at high temperatures. The addition of gelling additive strongly increases the viscosity. This change becomes critical at temperatures above 60°C, as the additive is starting to dissolve.

Injection moulding can be performed in a broad range of temperatures above the T_g, if it can be assured that the agarose is dissolved. Then, injection temperature is not a critical parameter affecting the properties of the green bodies if it is above the T_g of the gel-system and neither are the residence time nor the applied pressure. The obtained green densities were above 50%th. After sintering, homogeneous microstructures with final densities around 90%th were obtained.

Aqueous LPIM becomes a powerful low-cost effective method for producing complex shaped parts of silicon nitride by pressureless sintering.

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