

Improved consolidation of alumina by agarose gelation

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Abstract

A great effort has been devoted to develop low-cost effective forming methods for the production of complex-shaped parts. One of the most promising processes is low-pressure injection moulding in water in which a slurry gellates in the presence of a thermogelling binder. For this technique agarose has been found to be a suitable gelling additive. This work deals with the manufacturing of alumina by agarose gelation. For such purpose the rheological behaviour of aqueous alumina slips is studied as a function of the polyelectrolyte concentration, the solid loading and the temperature, in order to reproduce the injection conditions. The gelation behaviour of agarose solutions is studied from rheological measurements. Two different routes for preparing the injection slip are studied, the first by adding agarose as a solid powder and then heating the slurry, and the second by preparing independently the slurry and the agarose solution and further mixing at temperatures higher than 60°C. This second route demonstrates to be suitable for obtaining reliable alumina parts with a green density of 58% of theoretical and a sintered density of 98.7% of theoretical, significantly higher than the values reported in previous works. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Scaling-up of any shaping technique to industrial production depends on several factors, such as the piece geometry, the lot size, the homogeneity of the pieces and the process reliability.^{1–3} In addition, the development of cost-efficient and environmentally friendly processes constitutes a major objective for the new production technologies.⁴ These requirements are satisfied to a great extent by colloidal forming methods.^{5–7} They are based on the preparation of a stable, well-dispersed slurry in which the control of the colloid chemistry and the rheology makes possible to manipulate the interaction forces among the particles.^{8–10}

In conventional slips forming processes, the particles are dispersed in a low viscosity slurry and consolidate into a solid compact after liquid removal by filtration or evaporation. In contrast, other techniques are being investigated where the well-dispersed slurry is forced to

flocculate, coagulate or gelate so that the liquid is not removed but gellated.^{11–14} Much effort has been devoted in recent years to the study of forming processes based on the thermogelling properties of suitable binders. These systems are being successfully applied in the low-pressure injection moulding^{15,16} in which the conventional carrier polymers are substituted by an aqueous suspension. Several investigators have studied the effect of agaroid binders^{17–20} in ceramic processing, pointing out the low concentrations needed (typically about 1 wt.% referred to solids) and the high strength of the green bodies. Agar and agarose have been used for manufacturing alumina parts, but the high melting temperature of these binder (normally higher than 80°C)²¹ difficults processability because at those temperatures the dispersed particles tend to flocculate.

The final densities reported in previous works for agarose gelation are unexpectedly low comparing with the densities obtained by slip casting.^{18–20,22,23} The low concentration of additives should not promote this strong difference. Then, it must be thought that mixing step has not been yet optimised. It has been demonstrated elsewhere²⁴ that the same slurry prepared by different mixing/milling procedures can provide very different rheological properties. This effect is

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reinforced when the slips are heated at the injection temperature.^{23,25}

The purpose of this work is to optimise the rheological properties of aqueous alumina slurries at different temperatures and to improve the mixing efficiency when agarose is added as a gelling binder. Two mixing routes are investigated: firstly, the addition of agarose as a powder into the dispersed slip followed by heating the mixture; secondly, the addition of hot agarose dissolution into the hot ceramic slurry.

2. Experimental

As ceramic powder a commercial Al_2O_3 was used (Condea HPA05, Germany) with a mean particle size of 0.4 μm (measured by laser diffraction, Malvern, Mastersizer S, UK) and a specific surface area of 9.5 m^2/g (measured by N_2 adsorption, BET, Monosorb, Quantachrome, USA). Aqueous suspensions were prepared by ball milling for 6 h with alumina jar and balls. As deflocculant an ammonium salt of polyacrylic acid (Duramax D3005, Rohm & Haas, USA) was used at different concentrations from 0.5 to 1.5 wt.% referred to dry solids. The suspensions were prepared to solid loadings of 75 and 80 wt.% (43 and 50 vol.%, respectively). The resulting pH value is 9.0 ± 0.1 . These suspensions were shaken in closed flasks for 24 h prior to binder addition in order to reach an adequate surface equilibrium according to previous studies.²⁶

The rheological behaviour of the differently deflocculated slurries was studied using a rheometer (Haake RS50, Germany) operated at control rate mode. Measurements were performed with a double cone and plate system (60 mm in diameter, cone angle 2°) at temperatures ranging from 25 to 92°C .

Thermal gelation was promoted by adding a pure agarose (D1-LE, Hispanagar, Spain) as binder. Agarose was supplied as a powder with a mean particle size larger than 100 μm . The glass transition temperature (T_g) for a 2 wt.% solution of water is about 36°C . Both the melting and the gelling behaviour of the agarose was studied measuring the evolution of viscosity with temperature using a probe of temperature and maintaining a constant shear rate of 100 s^{-1} similar to the imposed shear during injection.²³ Viscosity data were continuously recorded on heating and further cooling.

The addition of agarose into the previously dispersed slip was performed by two different routes: Route 1, in which the agarose powder was added as supplied to the well-dispersed ceramic slurry. The mixture was homogenized by 2 h ball milling and then heated above 65°C . Route 2: an agarose solution was prepared at a concentration of 5.6 wt.% by dissolving the as-received agarose powder in water at high temperature ($>90^\circ\text{C}$) and subsequent maintenance at $T > 60^\circ\text{C}$. Then, the

required amount of hot agarose solution was added to the dispersed ceramic slurry heated at 65°C . Fig. 1 shows a flow chart of the two mixing procedures.

Injection of the slips was performed in a manual low-pressure injection moulding machine (Peltsmann MIGL28, USA) controlling the temperature in the tank and in the feeder pipe at 60°C . Residence times into the mould cavity were 10–20 s and a pressure of 0.4 MPa was applied. Steel moulds cooled by flowing water with cavity dimensions of $60 \times 10 \times 10 \text{ mm}$ were used. The as-injected bars were left in air for 48 h for drying. Sintering was performed at $1500^\circ\text{C}/2 \text{ h}$ in an electric furnace. Microstructural observations were performed by scanning electron microscopy on green and sintered fracture surfaces.

3. Results and discussions

3.1. Rheological properties of alumina slips

Fig. 2 shows the flow curves of alumina slips with 75 wt.% solids and different concentrations of polyelectrolyte at room temperature. A minimum viscosity is obtained for a deflocculant content of 0.8 wt.% and the pseudoplastic behaviour observed for the other concentrations becomes nearly Newtonian for that one. Slips prepared to a solid content of 80 wt.% showed a minimum viscosity also for 0.8 wt.% dispersant. The flow curves of 80 wt.% slips with 0.8 and 1.0 wt.% deflocculant are also shown in Fig. 2. Besides the deflocculation curves at room temperature, it has been demonstrated elsewhere^{22,23} that temperature can affect the adsorption state and hence the dispersing conditions so that a well-dispersed suspension can flocculate at higher temperatures. In this case more dispersant could help to maintain stability. Fig. 3 shows the evolution of slip viscosity (at 100 s^{-1}) with temperature for three dispersant concentrations and a solid content of 75 wt.%. It can be seen that the viscosity of the slip dispersed with 0.8 wt.% dispersant is lower at any temperature and slightly increases above 60°C . According to rheological characterisation, this was the concentration selected for further experiments.

The viscosity of suspensions with 80 wt.% solids was also studied as a function of temperature. The results for a shear rate of 100 s^{-1} are plotted in Fig. 4. The data corresponding to 75 wt.% slips with that dispersant concentration are also shown for comparison purposes. The concentrated slip follows the same trend with temperature but the higher concentration makes the viscosity to increase much more above 60°C . No reliable data could be obtained at higher temperature because the suspension destabilised leading to flocculation that can be expected to affect deleteriously the uniformity and mechanical response of the injected parts.

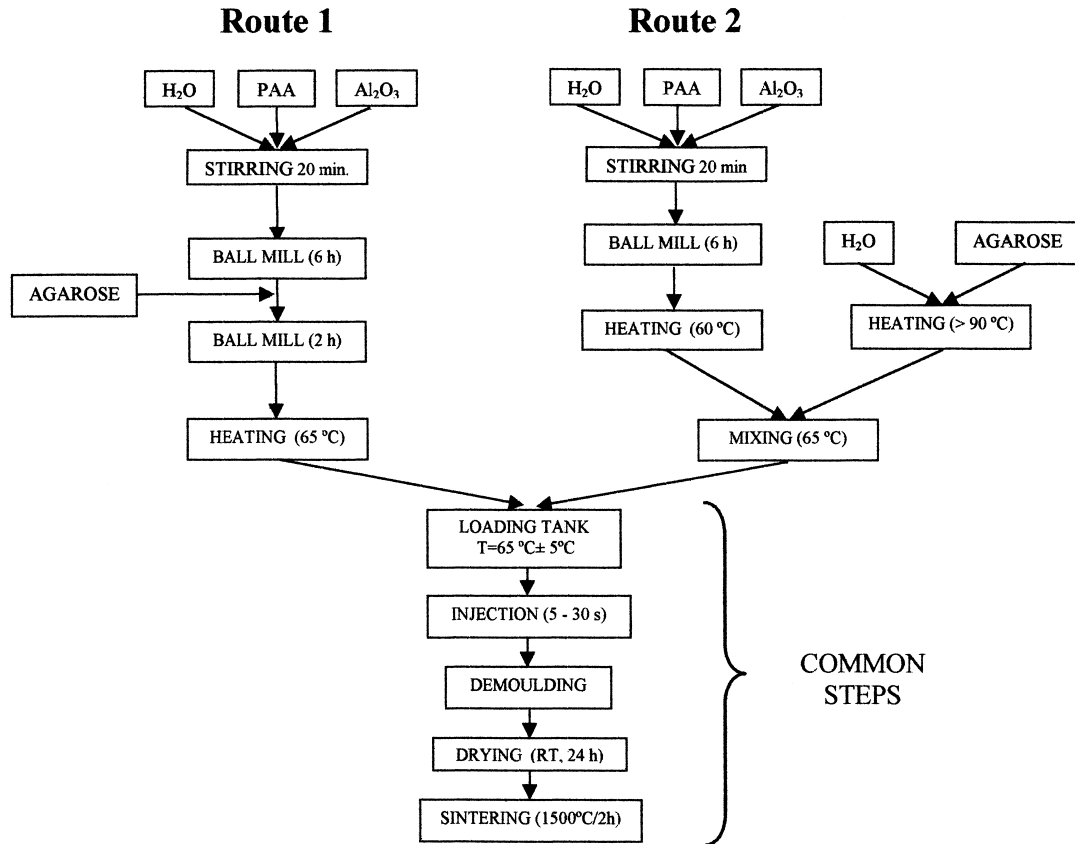


Fig. 1. Flow chart of the two processing routes.

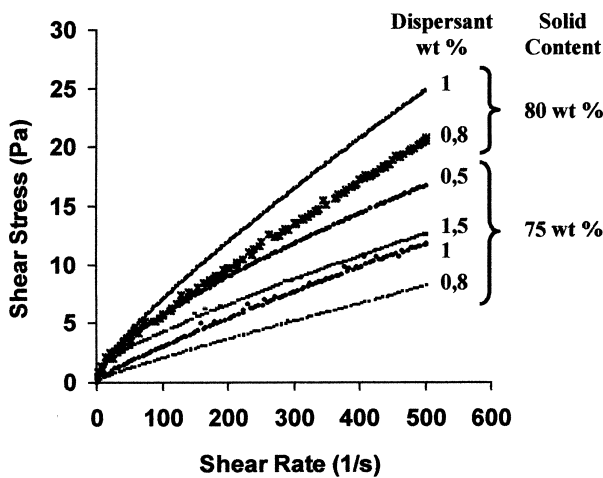


Fig. 2. Flow curves of 75 and 80 wt.% slips at different deflocculant concentrations.

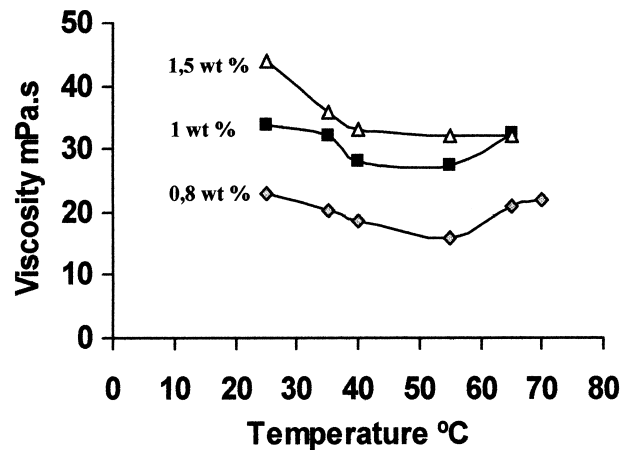


Fig. 3. Variation of viscosity with temperature of 75 wt.% slips at different deflocculant concentrations.

On the other hand, Figs. 3 and 4 showed the measured decrease of apparent viscosity with increasing temperature. In contrast with the direct viscosity measurements, polymeric stabilisers and polyelectrolytes tend to flocculate by polymeric bridging when heated. This apparent contradiction can be solved simply by considering the effect of temperature on water viscosity.

When doing so a plot of the relative viscosity (defined as the viscosity of the slip over that of the suspending liquid) versus temperature can be drawn. This plot is shown in Fig. 5, where it can be observed that viscosity always increases with temperature, as expected. In the case of 80 wt.% slips the increase above 55 °C is very sharp thus indicating that the slip becomes inhomoge-

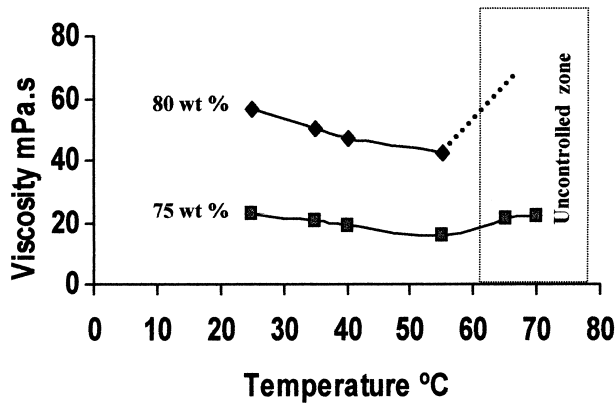


Fig. 4. Variation of viscosity with temperature of 75 and 80 wt.% slips for a deflocculant concentration of 0.8 wt.%.

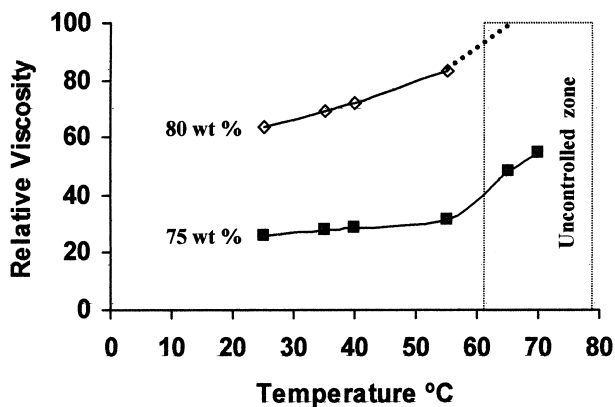


Fig. 5. Variation of relative viscosity with temperature of 75 and 80 wt.% slips for a deflocculant concentration of 0.8 wt.%.

neous and flocculates. A similar but less pronounced effect occurs also for 75 wt.% slips, but in this case the slip can be controlled up to 70°C.

This is an important consideration when adding agarose, since gelation takes place by bonding through the water molecules. At this point it must be noted that the addition of agarose as a powder should promote a further increase in viscosity and that it needs to be heated above 65°C to dissolve.

3.2. Characterisation of the gelling binder

To characterise the rheological properties of the gelling agent, aqueous solutions of agarose were prepared to a concentration of 2 wt.%. The continuous variation of viscosity with temperature was determined on heating from 25 to 92°C and subsequent cooling below 30°C. Fig. 6A and B shows the corresponding viscosity curves at a shear rate of 100 s⁻¹. There is a strong increase of viscosity on heating between 65 and 90°C with a maximum at 80°C (Fig. 6A), which gives the minimum temperature necessary for a complete dissolution (e.g. melting point). After that broad peak the viscosity decreases to the same values obtained before

reaching 60°C. On cooling (Fig. 6B) the viscosity slightly increases with decreasing temperatures until it peaks below 38°C, corresponding to the gelling point. There is an increase of viscosity of one order of magnitude in a temperature range as low as 5°C, thus indicating that a strong gel of agarose is being formed. The gel strength of a solution of 1.5 wt.% is higher than 1000 kg/cm² according to the datasheet provided by the supplier.

3.3. Characterisation of the injection slips

Injection slips were prepared according to the procedures shown in the flow chart of Fig. 1. In both routes the alumina was previously dispersed with 0.8 wt.% dispersant by 6 h ball milling.

In route 1, the agarose was added to the dispersed slurry in the form of the as-received powder in a concentration of 1 wt.%. Then the slip was heated. The addition of the binder powder promoted a big increase in viscosity. To avoid too high viscosities the slip with 75 wt.% solids was used. Fig. 7 shows the evolution of viscosity with temperature which is six times higher than that of the alumina slip without agarose. However, a similar evolution is recorded until 55°C where dissolution of agarose starts to occur thus making the viscosity to strongly increase. Since above 65°C the ceramic powder dispersion itself becomes very viscous, and considering the extra contribution associated to the agarose dissolution, there is a limiting working temperature at which the agarose is not completely dissolved although the slip maintains stable. Consequently, an excess of agarose is necessary to provide a high gel strength as a part remains undissolved producing heterogeneous microstructures and poorer sintering behaviour.

In route 2, the ceramic slurry and the agarose solution are prepared independently and heated independently too. This allows to completely dissolve the agarose powder at $T > 90^\circ\text{C}$. Nevertheless, the dissolution can be added to the slurry at lower temperatures as the viscosity of the agarose solution keeps constant during cooling up to around 40°C. In this way, a fluid solution is obtained that has not a significant influence on the rheological behaviour of the ceramic slurry. Hence, processing by route 2 allows to increase the solid loading of the slurry. In this work a concentration of 80 wt.% for the slurry has been proved to be suitable for an efficient injection process. However, after adding the agarose solution the total solids decrease to ~ 77.4 wt.%, only a little higher than in route 1. As the agarose is completely dissolved, the required concentration to form the network structure through water molecules can be also reduced. From these statements, a concentration of agarose of 1 wt.% referred to total water content was used for injection tests. This means that the concentration of gelling agent relative to dry solids is as low as 0.25 wt.%. Fig. 8 plots the variation of viscosity

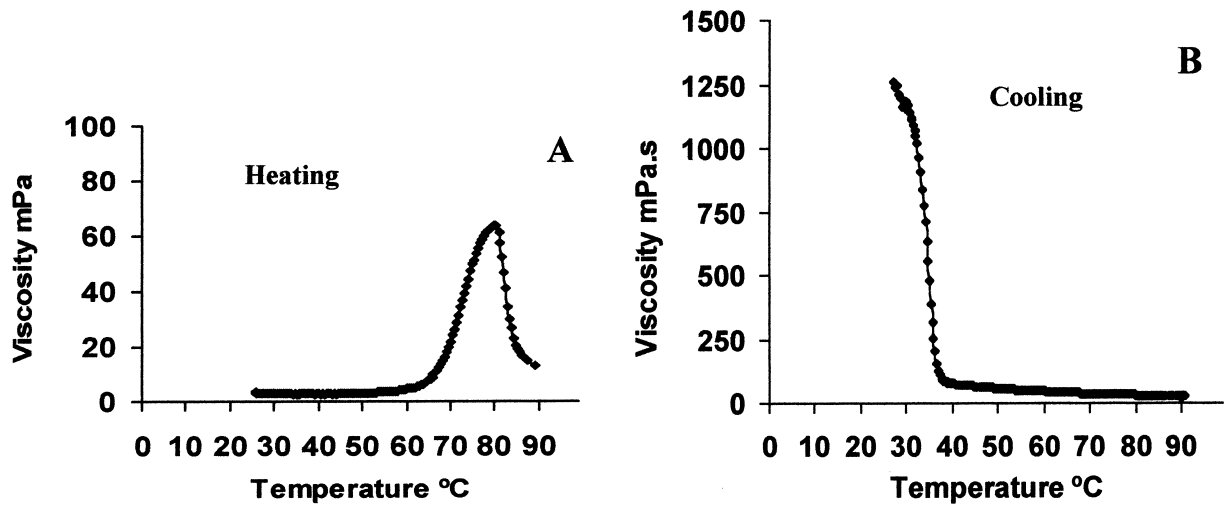


Fig. 6. Evolution of viscosity with temperature of a 2 wt.% solution of agarose.

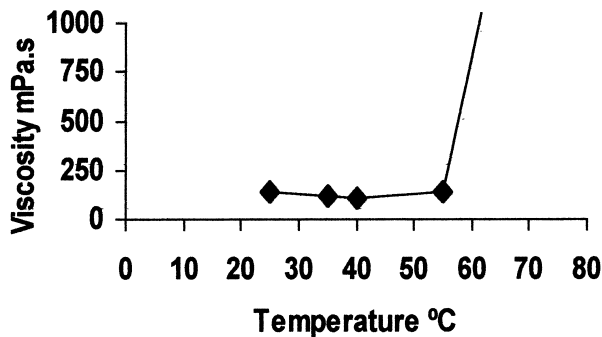


Fig. 7. Variation of viscosity on heating of the injection slip prepared by route 1 at a solid loading of 75 wt.%.

with temperature for the slip prepared by route 2. As the mixture is prepared after heating only the cooling behaviour is recorded. The viscosity value duplicates from 55 to 37 °C and then a very fast increase of viscosity takes place (from 0.5 to 1.4 Pa s between 37 and 30 °C).

Slips prepared with gelling agent by routes 1 and 2 were injection moulded at 0.4 MPa. The temperature of the mixtures was maintained at 65 °C and the moulds were cooled by flowing current water. A typical residence time in the moulds of 10 s was enough to assure a complete filling and gelation.

After drying at room conditions for 24 h, the density and shrinkage were measured. The slips mixed by route 1 provided after injection a green density of 2.14 g/cm³ (54% of theoretical) and a linear shrinkage of 5.85%. In the case of samples prepared by route 2 a green density of 2.26 g/cm³ (57% of theoretical) was reached. It must be noted that in this case the agarose was added as a solution, so the solid concentration of the final slurry decreased to 77.4 wt.%. The big differences in density can be also visualized in the corresponding green microstructures shown in Fig. 9. When agarose is com-

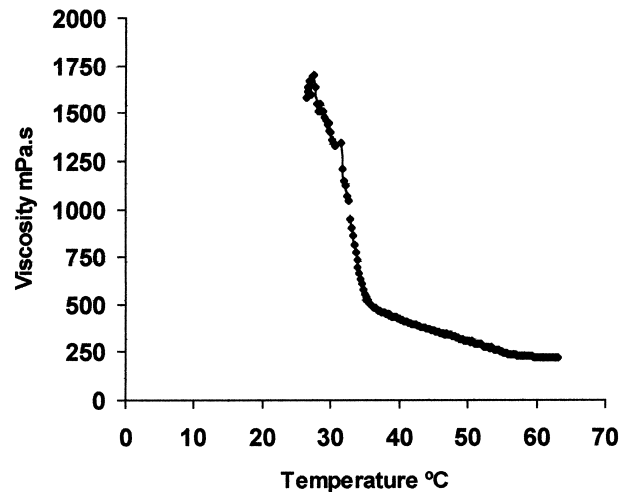


Fig. 8. Variation of viscosity on cooling of the injection slip prepared by route 2 at a solid loading of 80 wt.%.

pletely dissolved a very homogeneous microstructure is obtained whereas in the case of adding agarose as a powder some undissolved agglomerates still remain. These inhomogeneities will lead to lower densities and defects in the sintered bodies.

Sintering was performed at 1500 °C/2 h and the resulting densities were 3.74 and 3.92 g/cm³ (94.0 and 98.7% of theoretical) for the specimens prepared by routes 1 and 2, respectively, in good agreement with the properties of the green samples. Table 1 summarises the characteristics of the green and sintered bodies obtained according to both processing routes. The high final density obtained by route 2 demonstrates that the incorporation of the gelling additive is a critical parameter to be taken into account. A full dissolution of the gelling additive allows to avoid the presence of residual binder agglomerates and to reduce the concentration necessary for gelling.

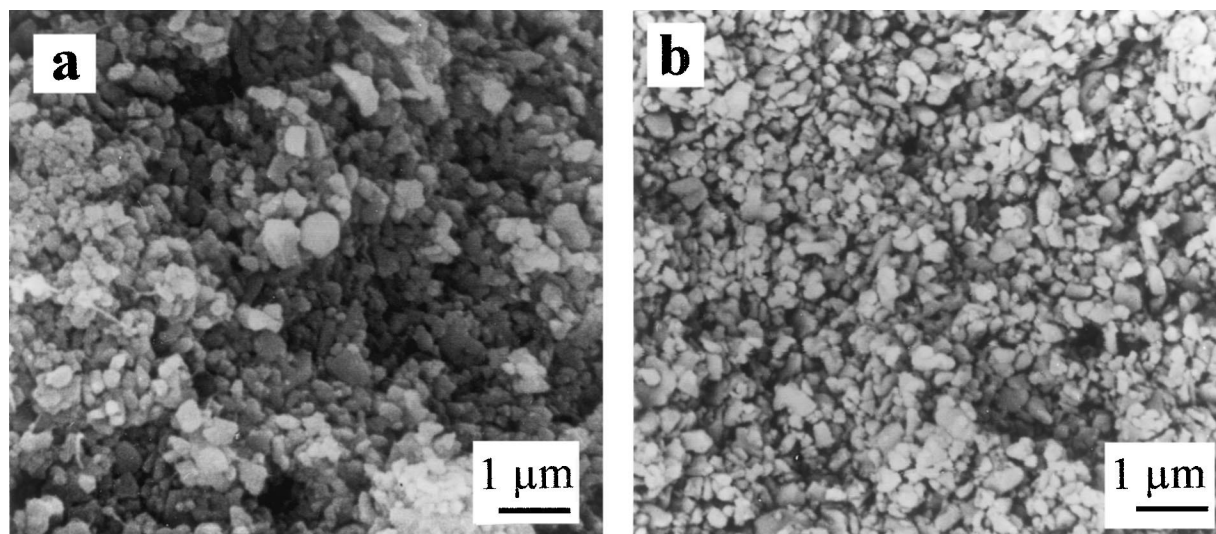


Fig. 9. Green microstructures of alumina injected samples prepared by routes 1(a) and 2(b).

Table 1
Properties of the slurries and the specimens prepared by routes 1 and 2

	Solid content	$\eta_{55^\circ\text{C}, 100 \text{ s}^{-1}}$ (mPa s)	Green density (g/cm ³)	Sintered density (g/cm ³)	Linear shrinkage (%)
Route 1	75 wt.% 43 vol.%	142	2.14 (54% of theoretical)	3.74(94% of theoretical)	23.2
Route 2	80 wt.% 50 vol.%	248	2.26 (57% of theoretical)	3.92(98.7% of theoretical)	19.2

4. Conclusions

As in any other colloidal processing technique, a basic requirement for aqueous LPIM is to prepare a stable, well-dispersed ceramic slurry. Furthermore, stability depends also on the temperature, so the rheological properties at different temperature conditions must be studied and controlled. In the case of the selected alumina powder stable slips can be prepared at solid concentrations of 80 wt.% (50 vol.%) by dispersing with 0.8 wt.% polyelectrolyte.

The second aspect to be considered is the way in which the gelling additive is incorporated. Strong differences in viscosity and in the final properties of the injected bodies are found depending on the route followed to add the gelling. For the agarose powder used in this study it has been shown that the addition as a powder limits the solid loading due to the strong increase in viscosity. The slip starts to flocculate at temperatures around 65°C, where the agarose cannot fully dissolve. A green density of 54% theoretical is obtained by this route and the sintered density is relatively low (94% of theoretical) due to the presence of agarose undissolved agglomerates.

Much better results are obtained when the agarose is fully dissolved prior to the incorporation into the ceramic slurry. In this case, the green density is 57% of the-

oretical and the absence of binder agglomerates allows to reach a sintered density as high as 98.7% of theoretical. A further advantage of this mixing route is that when all the additive is dissolved the quantity necessary to promote gelation can be significantly reduced. In this work a concentration of 0.25 wt.% agarose referred to solids has demonstrated to be enough to obtain higher sintered densities than those reported previously in the literature.

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