February 2001

Materials Letters 47 (2001) 324–328

MATERIALS LETTERS

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# Aqueous injection moulding of alumina using agarose

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Received 21 February 2000; received in revised form 26 July 2000; accepted 31 July 2000

## Abstract

Injection moulding in water is receiving great interest for the low-cost production of near-net-shaped ceramic parts. In this technique, aqueous suspensions are gelated in the presence of a low concentration of gelling additive. In this work, alumina bodies are injection moulded in water by adding 1 wt.% agarose. The agarose is incorporated to the previously dispersed slurry and the blend is then milled in a ball mill. Agarose dissolves upon heating, but the dispersed slurry maintains stability up to 70°C. Rheological behaviour is studied as a function of temperature for the ceramic slurry with and without agarose. The injected parts show a homogeneous microstructure without binder agglomerates. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Alumina; Aqueous injection moulding; Agarose gelation; Rheology

## 1. Introduction

Aqueous injection moulding is receiving great attention in the manufacture of near-net-shaped ceramic components [1–4]. The substitution of carrier polymers by water is an emerging goal due to the health and environmental benefits. Studies on the shaping of ceramic parts with small quantities of gelling binder, typically about 1 wt.% referred to dry solids, has been reported [3–6]. Among the different gelling additives, the one that has shown better gelling properties is agarose.

The process in water has some particularities that must be taken into account. The most significant one is related to the fact that the slurry must be heated prior to injection and the binder must be well homogenized to avoid the presence of agglomerates. As in any other colloidal processing route, the main requirement for obtaining a homogeneous production deals with the necessity to prepare a stable, well-prepared suspension [7,8]. However, when temperature increases, some flocculation by polymeric bridging can occur when slips are dispersed with polymeric stabilizers or polyelectrodes [9,10]. On the other hand, even if the slip is stable at the injection temperatures, a further problem can appear when the binder is incorporated to obtain a homogeneous blend.

In previous work [11], the authors studied the rheological behaviour of alumina slips prepared by different milling/mixing procedures, where the agarose was previously dissolved, left to gel and crushed. The granulated agarose so obtained was then added to the preheated alumina slurry at above

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PII: S0167-577X(00)00258-5

60°C and then the mixture was injected. However, the green bodies showed the presence of agarose agglomerates that were not broken down. As a result, some defects were detected in the sintered microstructure due to those binder agglomerates.

The present work aims to optimize the mixing step by incorporating the agarose in the alumina aqueous slip as a powder and heating the mixture for injection further, in order to avoid agglomeration of the agarose.

## 2. Experimental

Commercially available alumina powder, (Alcoa CT3000SG, Germany) with specific surface area of 7.8 $m^2/g$ (measured by $N_2$ adsorption, BET, Monosorb, Quantachrome, USA) and average particle size of 0.6 μm (measured by laser diffraction, Malvern, Mastersizer S, UK) was used in the present study. Aqueous slips were prepared to a solid loading of 75 wt.% (43 vol.%) by using an ammonium salt of acrylic polymer (Duramax D-3005, Rohm and Haas, USA) as deflocculant. It is supplied as an aqueous solution containing 35% active matter, and has a molecular weight of 2500 Da.

Slips were prepared with dispersant contents between 0.5 and 1.5 wt.% (referred to dry solids), that correspond to 0.17–0.53 wt.% of active matter and, taking into account the powder surface, to 0.224–0.673 mg of dispersant/$m^2$ of alumina powder surface. The slips were maintained under agitation for 24 h to assure an equilibrium state.

The rheological characterization of these slips was performed using a rheometer (Haake, Rheostress RS50, Germany) operating at controlled rate with concentric cylinders. The flow curves of each slip were determined for the temperatures ranging from 25°C to 70°C. The viscosity–temperature curves were drawn corresponding to a shear rate of 100 $s^{-1}$.

When the dispersing conditions of slips as a function of temperature were optimised, the binder was added. An agarose powder (Hispanagar D1-LE, Spain) was used as a binder. The powder was added to the slip and milled/mixed for 4 h in an alumina ball mill. After milling, the mixture was heated to 70°C and maintained at that temperature. A binder concentration of 1 wt.% relative to alumina powder was added.

Injection tests were performed in a manual LPIM machine (Peltsmann MIGL28, USA). The temperature in the tank and in the orifice, and the residence time of the slip into the mould cavity between 10 and 20 s, were maintained during the tests. The applied injection pressure was 0.4 MPa. A steel mould cooled by flowing water was used to produce the test bars of 60 × 10 × 10 mm dimensions. These pieces were left in air for drying. The green densities of samples were measured by Hg immersion. Sintering was performed at 1600°C for 2 h and the final density was measured by immersion in water. Scanning electron microscopy was performed on fracture surfaces for green and sintered specimens.

## 3. Results and discussion

The flow curves were obtained for all the slips at shear rates ranging from 0 to 500 $s^{-1}$ at different temperatures. Fig. 1 shows the flow curves of slips with different deflocculant concentrations at a temperature of 25°C. A shear-thinning behaviour is observed in all cases with a minimum viscosity for the slip dispersed with 0.8 wt.% deflocculant.

Afterwards, the effect of temperature on the slurry viscosity was studied for those concentrations of dispersant. Fig. 2 shows the variation of viscosity vs. temperature of slips containing concentrations of deflocculant of 0.5, 0.8 and 1.0 wt.% at a shear rate of

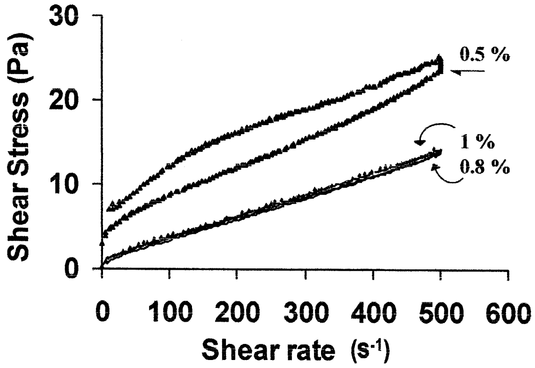

Fig. 1. Flow curves of 75 wt.% alumina slips with different deflocculant concentrations at 25°C.

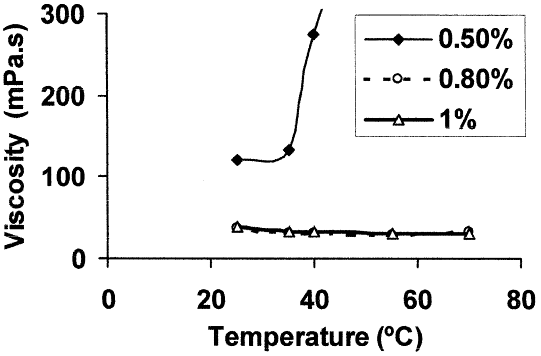

Fig. 2. Variation of viscosity vs. temperature of slips containing concentrations of deflocculant of 0.5, 0.8 and 1.0 wt.% at a shear rate of 100 $s^{-1}$.

100 $s^{-1}$, because this is the approximate shear rate at which the injection process being carried out. A significant increase in viscosity is observed for 0.5 wt.% of dispersant with an increase in temperature. This is because the concentration of deflocculant is not sufficient to reach the saturation limit of adsorption at temperatures above 35°C, and the slurry starts to flocculate by polymeric bridging. In the slips containing higher concentrations of dispersant (0.8 and 1.0 wt.%), the viscosity remains nearly constant in the whole temperature range. In order to assure a low viscosity with a consistent rheological behaviour during the injection process, a concentration of 1 wt.% of deflocculant is selected.

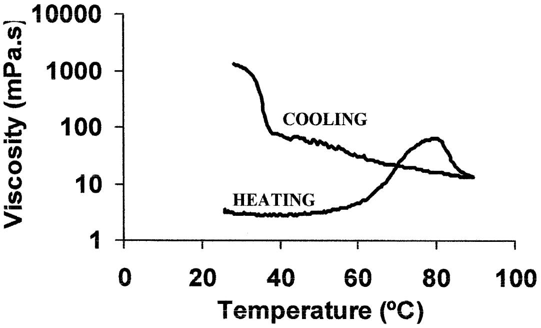

Fig. 3. Continuous variation of viscosity vs. temperature of injection slips containing 1.0 wt.% dispersant and 1.0 wt.% agarose, both referred to dry solids.

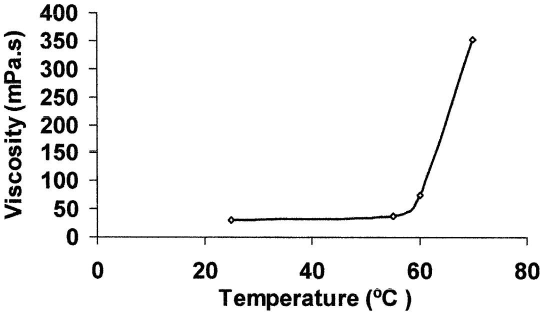

Fig. 4. Variation of viscosity vs. temperature of injection slips containing 1.0 wt.% dispersant and 1.0 wt.% agarose, both referred to dry solids.

After selecting the most suitable dispersing conditions, aqueous solutions of gelling binder were prepared to a concentration of 2 wt.%. The evolution of viscosity with temperature was continuously recorded using the rheometer connected to a temperature probe. Fig. 3 shows the variation of viscosity of the agarose solution during both the heating and the cooling processes. According to these curves, the increase of viscosity in the range between 650°C and 80°C during heating is related to the dissolution of agarose in water, and indicates that it is necessary to arrive at this temperature if a full dissolution of the binder is desired, in order to increase the efficiency of gelation. The observed change of viscosity in the cooling curve at around 37°C corresponds to the binder $T_g$, indicating the gelling temperature at this concentration. According to these data, after dissolution of agarose powder, the working range of temperatures for injection applications is 45–60°C.

After adding the agarose, the slurry dispersed with 0.8 wt.% deflocculant presented a much higher viscosity. So concentrations of 1 wt.% were necessary for a reliable processing. The viscosity behaviour with temperature of the alumina slip mixture with 1 wt.% of agarose (related to alumina powder) is shown in Fig. 4. The evolution of viscosity follows the same trend that of the agarose solution,

Table 1
Characteristics of the injected alumina samples

| Density (%Th) | | Linear shrinkage (%) | |
|---|---|---|---|
| Green | Sintered | Green | Total |
| 51.5 | 92.2 | 10 | 26.5 |

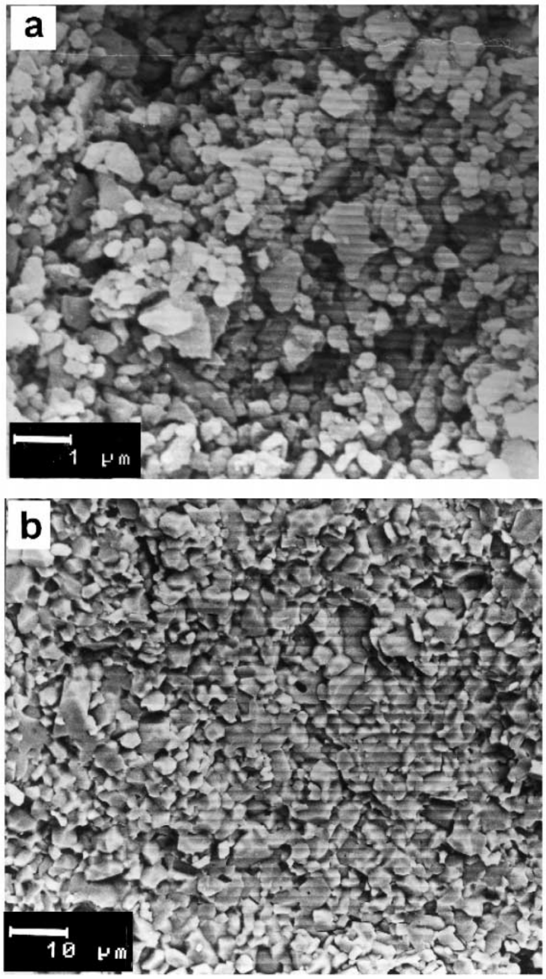

Fig. 5. SEM microstructure of alumina samples obtained by aqueous injection moulding in the green state (a) and after sintering (b).

confirming that at temperatures above 60°C, the agarose powder starts to dissolve.

Table 1 summarizes the green density and linear shrinkage of the injected green bodies and after sintering at 1600°C/2 h. The obtained values are very similar to those presented in a previous work [11]. However, the differences in the procedure followed to incorporate the agarose between the present and the previous work strongly influence the resulting microstructure. Fig. 5a and b shows the SEM microstructures of green and sintered alumina samples obtained by aqueous injection moulding. They show a high homogeneity without any agglomerates of the gel. Therefore, it can be concluded that the incorporation of agarose as a powder in the slip improves the homogeneity of samples, although some porosity still remains.

## 4. Conclusion

Stable alumina slips have been prepared by using a concentration of polyacrylic acid-based polyelectrolyte of 0.8–1.0 wt.%. The stability is maintained in the range of temperatures used for injection (up to 70°C). However, only after the addition of agarose does the suspension containing 1 wt.% dispersant becomes more suitable for injection.

The incorporation of the gelling additive is a critical step for the production of homogeneous pieces. In this work, agarose has been incorporated as a powder to the previously homogenized slip. The mixture has been milled and subsequently heated at 70°C to dissolve the agarose. The microstructural observations of the test bars demonstrate that no agglomerates of agarose are detected; whereas in the case of hydrated agarose (as reported in Ref. [11]), some agglomerates remain in the green body.

## Acknowledgements

This work has been supported by CICYT (Spain) under contract (MAT97-0676). The authors thank to D. Rafael Armisen (Hispanagar, Spain) for the agarose supply and helpful discussions. A.J. Millán thanks CONICIT (Venezuela) for the concession of a grant.

## References

[1] L.M. Sheppard, Am. Ceram. Soc. Bull. 68 (1989) 1815–1820.
[2] R. Moreno. Bol. Soc. Esp. Ceram. Vidrio (in press).
[3] A.J. Fanelli, R.D. Silvers, W.S. Frei, J.V. Burlew, G.B. Marsh, J. Am. Ceram. Soc. 72 (1989) 1833–1836.
[4] Z.S. Rak, P.J. van Tiborg, in: G. Ziegler, H. Hausner (Eds.), Euro-Ceramics: II. Basic Science and Processing of Ceramics, vol. 1, DKG, Berlin, Germany, 1991, pp. 409–413.
[5] Z.S. Rak, F.W. Hamburg, Ceram. Acta 7 (1995) 5–13.

[6] T. Zhang, S. Blackburn, J. Bridgwater, Br. Ceram. Trans. 96 (1994) 229–233.

[7] F.F. Lange, J. Am. Ceram. Soc. 72 (1989) 3–15.

[8] R.J. Pugh, in: R.J. Pugh, L. Bergström (Eds.), Surf. Colloid Chem. Adv. Ceram. Process., Marcel Dekker, New York, USA, 1994, pp. 127–192.

[9] N.S. Bell, L. Wang, W.M. Sigmund, F. Aldinger, Z. Metallkd. 90 (1999) 388–392.

[10] A.J. Millán, M. Bravo, R. Moreno, M.I. Nieto, Bol. Soc. Esp. Ceram. Vidrio 38 (1999) 93–99.

[11] A.J. Millán, R. Moreno, M.I. Nieto, Br. Ceram. Trans. (in press).