Journal of the European Ceramic Society 20 (2000) 1115–1119

Gelcasting of alumina from acidic aqueous medium using acrylic acid

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Received 13 May 1999; received in revised form 16 August 1999; accepted 12 September 1999

Abstract

An aqueous gelcasting process for alumina using an acrylic acid monomer has been investigated. Concentrated aqueous alumina slurries with pH 3 were set in moulds at 80°C during 10–15 min by polymerisation of the monomer contained in it using ammonium persulphate as free-radical initiator. The green density maximum (57% TD, corrected for organic content) was obtained at ~6 wt% binder content, at which the green strength (by diametrical compression test) measured was 11.5 MPa. The green bodies with binder content ⩾4 wt% were amenable to conventional machining operations such as lathing, milling and drilling. The total linear shrinkage of 55 vol% A16SG alumina slurry was 1.4% during drying and 15–17% during binder removal and sintering to 97% TD.

Keywords: Al_2O_3; Gelcasting; Shaping; Suspensions

1. Introduction

Gelcasting is a novel ceramic forming process by which complex, machinable and near-net- shape ceramic green parts are produced by casting aqueous or non-aqueous concentrated ceramic slurries containing organic monomers and setting the slurry in a mould by in situ polymerisation of the monomers.[1–4] The process has shown several advantages over widely used injection moulding process using ceramic powder- thermoplastic polymer blends. For example, the pourable gelcasting slips are easy to handle for mould filling when compared to the hot viscous systems those used in the injection moulding process. In addition, the gelcasting process allows the binder to be used in small quantities and thereby avoids long and complicated binder burnout schedule.

An aqueous gelcasting system is preferred to a non-aqueous system since use of water as solvent brings gelcasting closer to traditional ceramic processing, makes drying easier and avoids environmental problems associated with disposal of spent organic solvents. However, the monomers used in the conventional aqueous systems, in which the ceramic powder is dispersed at pH ~9 using a polyacrylate dispersant, have been limited to using acrylamides and certain selected acrylic esters. While the acrylamide monomer being toxic suffer hesitation from industries, some of the esters require co-solvents to bring about homogeneous solution. In this context, simple acrylic acid monomers are interesting since they are less toxic compared to acrylamide monomers and highly water soluble as well. In addition, strong particle-to-polymer and polymer-to-polymer interaction through the carboxylic acid group of the acrylic polymer would provide strong green bodies.[5] But, in the conventional gelcasting slurry, the use of acrylic acid is restricted since excess electrolyte generated while adjusting the slurry pH to alkaline brings unfavourable changes in slip's flow properties. Powder dispersion in acidic aqueous medium is an alternate approach to overcome the above problem.

Mineral acids have been widely used for preparation of aqueous dispersions of alumina.[6] Highly concentrated (> 55 vol%) slurry with viscosity less than 1 Pa s, as desired for gelcasting, has been possible by a treatment of the powder with hydrolysed aluminium and the slurry has been used for gelcasting using a non-acrylic monomer.[7,8] The results of our investigation on gelcasting of alumina using acrylic acid are reported in this paper.

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PII: S0955-2219(99)00244-7

2. Experimental

α-Alumina powder was A16SG (ACC-Alcoa Ltd., India) with an average particle size of 0.34 mm and BET surface area of 10.4 m^2/gm. The powder was treated with hydrolysed aluminium using the procedure reported elsewhere.[7] In this procedure hydrolysed aluminium is produced in situ in a 80 wt% alumina slurry from aluminium nitrate (2.5 wt% of alumina) using stoichiometric amount of hexamethylene tetramine (HMTA) as the base generator. The hydrolysis is carried out at ambient temperature over a period of 48 h during which the slurry pH increases from 4 to 5. The resulting mix, after adjusting its pH to 4, is aged for 12 h. The treated powder is centrifugally separated, washed with water and dried at a temperature below 80°C to retain a moisture content about 1%. Acrylic acid (Purum grade, 99%, Fluka, Switzerland) was used after distillation.

The flow chart of the present gelcasting process is shown in Fig. 1. The gelcasting slurry (55 vol% solids) was prepared by dispersing alumina by machanically stirring in desired volume of an aqueous premix solution containing acrylic acid and ammonium persulphate. The pH of the slurry thus prepared was about 3. The mixing container was kept in an ice bath so that the slurry temperature was kept below 10°C during mixing and degassing. The slurry was then cast in glass or aluminium moulds and gelled by keeping the moulds in an air oven at 80°C. The gelled body was removed from the mould and dried first in humidity controlled chambers to remove $>95\%$ of the water content and then in an air oven at 80°C. The composition of the premix solution was varied such that the amount of acrylic acid in the slurry could be varied in the range of 2–10% by weight of alumina. The amount of ammonium persulphate was kept at 0.3 wt % of the monomer. Cylindrical specimens with diameter in the range 10–25 mm and length measuring over 30 mm were prepared.

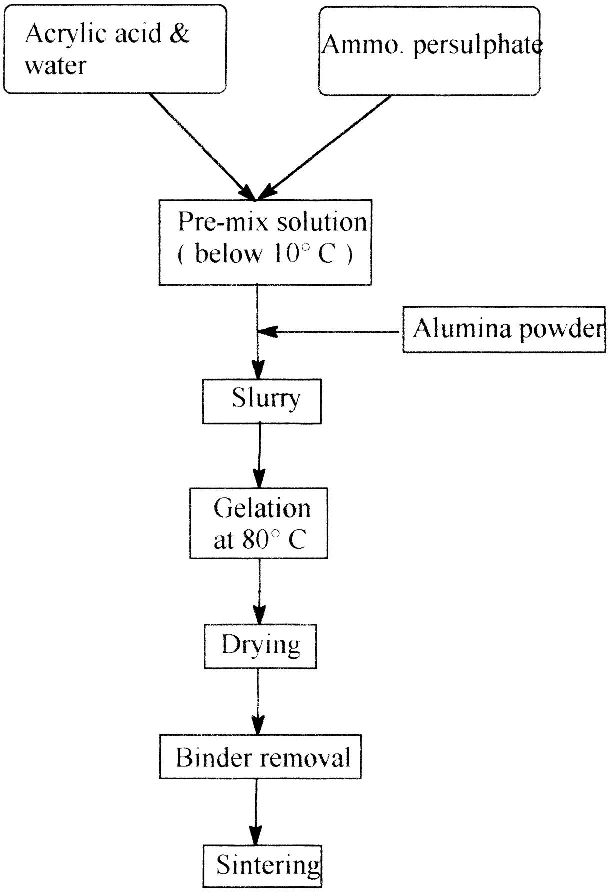

Fig. 1. Flow chart of the aqueous gelcasting process for alumina using acrylic acid.

The apparent viscosity of the slurries was measured in a Brookfield Synchrolectic viscometer (RVT/HBT model) using small sample adapter of coaxial geometry (SC4-21/13R). The densities of the green bodies were calculated from the volume measured by a mercury displacement method. The green strength was measured by a diametrical compression test in an instron testing machine (model 1195) using cylindrical specimens ($d=10$ mm, $h=4$ mm) and employing a loading rate of 0.5 mm/min.[5] Machinability of the green bodies was tested by turning, milling and drilling using conventional equipment and tools.

The binder burnout profiles of the gelcast samples in air/nitrogen at dynamic conditions were obtained by standard thermogravimetric analysis (TGA) using Dupont Thermal Analyst 2000. The green bodies were debinderised in a furnace by pyrolysis of the binder in static air atmosphere by employing a heating rate of $\leqslant 1$°C/min from ambient to 600°C. The debinderised bodies were sintered at 1550°C for 2h by applying a heating rate of 10°C/min from 600°C to the sintering temperature.

3. Results and discussion

Mineral acids can promote polymerisation of acrylic monomers by cationic polymerisation mechanism.[9] In the gelcasting slurry, polymerisation of acrylic acid was found accelerated such that the slurry viscosity increased rapidly with time and gelation occurred within an hour at ambient temperature ($\sim$30°C). However, by keeping the slurry at a temperature below 10°C, polymerisation of the monomer could be retarded so that it remained fluid during mixing, degassing and casting. Fig. 2 shows the viscosity at various shear rates of a typical gelcasting slip measured at $\sim$8°C. The slurry exhibited shear thinning flow behaviour and the viscosity at 93 s^{-1} was less than 1 Pa s as desired for gelcasting slips.

Although gelation of the slurries could be achieved at ambient temperature, even in the absence of an externally added initiator, the gelled bodies showed poor handling strength for lack of sufficient molecular weight of the polymer. Therefore, it was necessary to enhance the degree of polymerisation by free-radical polymerisation of the monomer at an elevated temperature (80°C) using ammonium persulphate as initiator. The gelled bodies thus prepared had sufficient strength to withstand the mechanical stresses during mould removal and handling.

Gelled bodies in general are dried in humidity controlled chambers since rapid drying would cause the samples to warp or crack due to non-uniform shrinkage.[10] Fig. 3 shows a typical humidity controlled drying profile of a 30 mm long cylindrical specimen with a diameter of 25 mm. A near steady state removal of more than 95% of the moisture was achieved at ambient temperature by employing relative humidity values of 90, 80 and 65% successively for different periods. However, a faster drying rate than used in the present study may be possible, especially after removal of 30% of the moisture, since shrinkage of the sample was found almost ceased at this stage. The samples were finally dried in an air oven at 80°C for 24 h. The average linear shrinkage during drying was 1.4%. Fig. 4 shows the photograph of alumina green bodies of different shapes prepared by the present gelcasting process.

The effect of polymer content on the green density (corrected to organic content) and strength of the gelcast samples is shown in Fig. 5. The density maximum was obtained at a polymer content of ~6 wt%. The green strength, on the other hand, increased more or less linearly with the binder content up to 8 wt% and tended to level off at a binder content beyond 10 wt%. The density maximum obtained was 57% TD at which

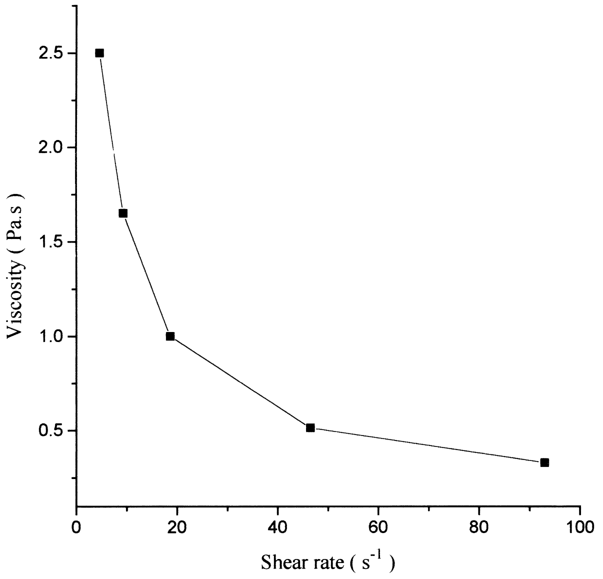

Fig. 2. Viscosity vs shear rate plot for the gelcasting slip with alumina, 55 vol%; acrylic acid, 6 wt% and pH 3.

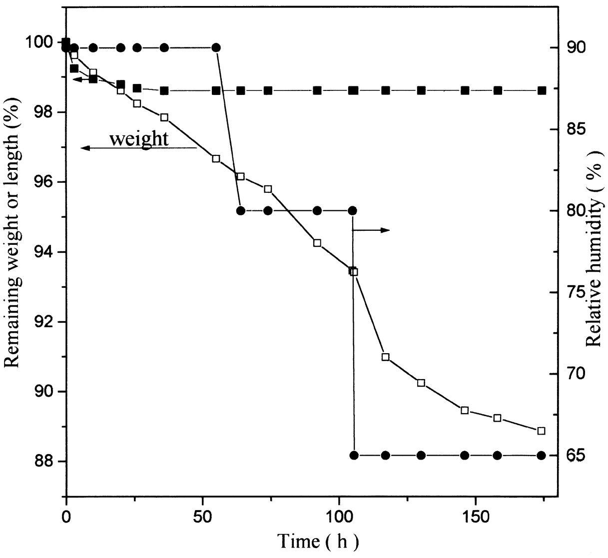

Fig. 3. Humidity controlled drying profile at ambient temperature of a cylindrical gelcast body (d=25 mm; h=30 mm) showing change in weight and length of the specimen with time.

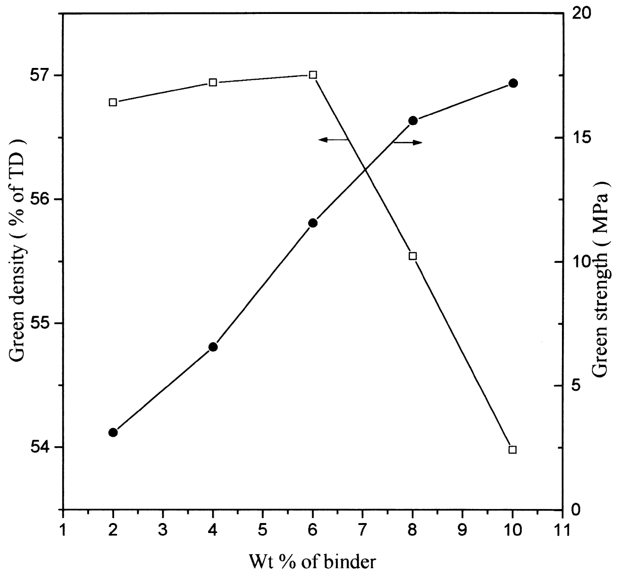

Fig. 4. Effect of binder content on the density and diametrical compressive strength of gelcast alumina green bodies.

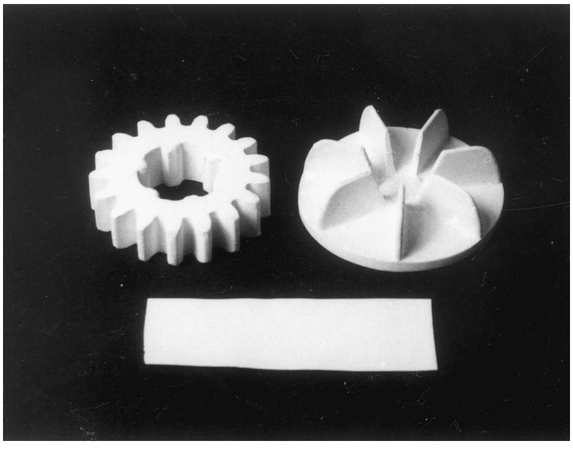

Fig. 5. Photograph of gelcast alumina green bodies of a spur gear (d=41 mm, h=12 mm), a fan-blade assembly and a 0.2 mm thick tape.

the strength measured was 11.5 MPa. On the other hand, the green bodies with binder content ⩾4 wt% showed good machinability characteristics. Fig 6 shows the photograph of a machined cylindrical green body. The body was lathed to form recessed steps, drilled to form a centre cavity and milled to form a groove using conventional equipment and tools.

Acrylic binders have been used for preparation of machinable alumina green bodies by compaction of the powder-binder blends at high pressures.[5] A green strength of 6.5 MPa was reported for the compacts with a density of ~57% TD and containing 5 wt% binder. Its gelcast counterpart exhibited a higher green strength as can be seen from Fig. 4. This may be attributed to fine dispersion of the powder in a continuous network of the binder that possible in the gelcast samples by in situ polymerisation of the monomer; in addition to enhanced binder-to-ceramic interaction and binder-to-binder interaction (inter-chain hydrogen bonding) that brought about through carboxylic acid of the polymer.

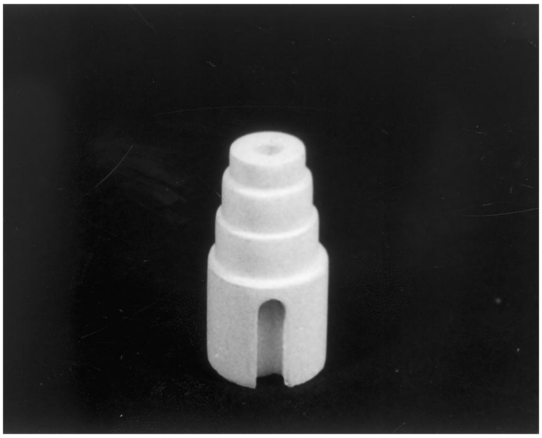

Fig. 6. Photograph of a machined alumina green body with 6 wt% binder showing recessed steps by lathing, a centre cavity by drilling and a groove by milling.

Fig. 7 shows the results of TGA of a gelcast sample in air and nitrogen atmosphere at a heating rate of 10°C/min. The weight loss that observed below 120°C is due to removal of residual water in the sample. The initial stage of decomposition of the polymer that occur between 120 and 200°C is due to elimination of water by inter and intra-molecular anhydride formation through the carboxyl groups. At higher temperatures, the binder burnout occur by depolymerisation and oxidative decomposition.[11] The binder burnout in nitrogen takes place at a lower rate than in air, particularly at temperatures above 350°C in the present case, since inert atmosphere suppress the oxidation potential and retard oxidative decomposition of binders.[12]

The binder removal profile constructed using conventional TGA in air at a heating rate of 1°C/min is shown in Fig. 8. The bulk of the binder (74%) was removed at temperature between 200 and 390°C where the average rate of binder loss was 0.39% per minute. Seventeen percent of the binder loss occurred below 200°C and 9% above 390°C with an average binder removal rate in the range 0.07–0.1% per minute. Therefore, by maintaining a heating rate of 1°C/min from ambient to 200°C and from 400 to 600°C, a lower heating rate of 0.5°C/min was applied for debinderisation of cylindrical specimens ($h=3$ cm, $d=2.5$ cm) in a furnace to avoid the possibility of producing defects in the samples during binder removal. Visible cracks or blistering were not observed in the samples.

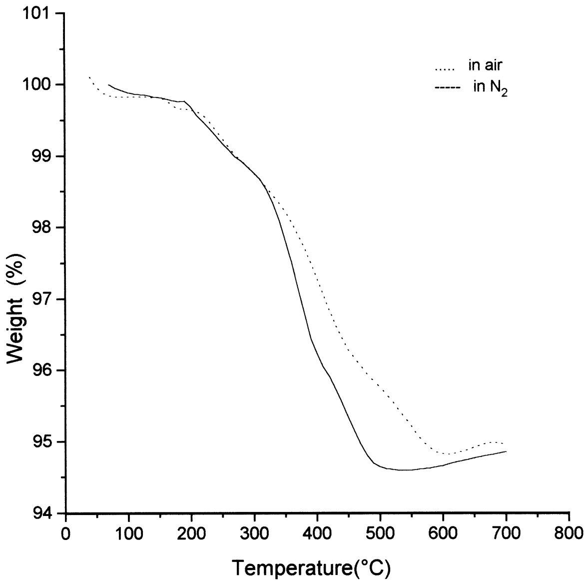

Fig. 7. TGA of a gelcast alumina green sample in air and nitrogen atmosphere at a heating rate of 10°C/min.

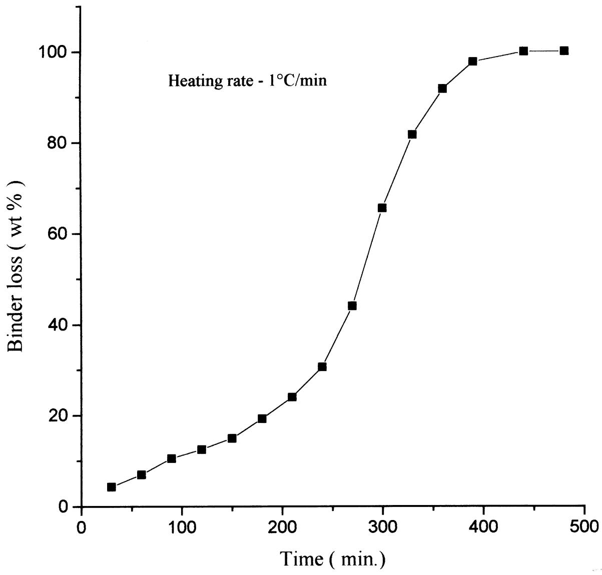

Fig. 8. Binder burnout in air vs time plot for a gelcast alumina green sample at a heating rate of 1°C/min.

The debinderised bodies those were sintered at 1550°C for 2 h showed a density of 97% TD. The shrinkage during sintering was isotropic and averaged 15 to 17%.

4. Conclusions

Acrylic acid could be used in an acidic aqueous concentrated alumina slurry for gelcasting of alumina. The slurry temperature was kept below 10°C in order to retard polymerisation of the monomer during mixing and degassing and thus to retain its flow properties for casting. Though the slurries can be gelled at ambient temperature, strong gels and green bodies were obtained by gelation at 80°C using ammonium persulphate as free-radical initiator for polymerisation. Dense, strong and machinable near-net-shape green bodies can be prepared by using a binder content of 4–6% by weight of alumina. The green bodies can be thermally debinderised by employing appropriate heating rates from ambient to 600°C. The total linear shrinkage of 55 vol% A16SG alumina slurry was 1.4% during drying and 15–17% during sintering to 97% TD.

Acknowledgements

One of the authors, K.P., is thankful to CSIR for awarding a Senior Research Fellowship during the tenure of this work.

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