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Gelcasting of alumina using urea-formaldehyde II. Gelation and ceramic forming

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Abstract

A new aqueous gelcasting system for alumina was investigated. Concentrated (55 vol%) aqueous ceramic slurries dispersed using a mineral acid was gelled by pH controlled condensation polymerisation of methylolurea monomers derived from urea and formaldehyde. Gelation of the slurry occurred at ambient conditions during 30–80 min at pH 2.5–3. Humidity controlled drying of gelled bodies prepared using alumina of average particle size of 0.34 μm yielded green bodies with density of 57% (corrected for organic content) of theoretical density and strength (by diametrical compression test) of 0.35 MPa at polymer content ~6% by weight of alumina. Debinderization of the green bodies was accomplished by pyrolysis in air below 350°C. The relative density of the bodies sintered at 1550°C for 2 h was 97% TD and the shrinkage during sintering was isotropic and averaged 14 to 16%.

Keywords: A. Suspensions (aqueous); D. Al_2O_3; Gelcasting

1. Introduction

Gelcasting is a novel ceramic forming process for making complex-shaped ceramic parts [1–4]. The conventional aqueous process follows dispersion of ceramic powder in a water-based monomer solution using polyacrylate dispersants at pH ~9 and setting the slurry in a mould by means of free-radical initiated polymerisation of monomers. However, the process has been limited to using a few selected acrylic monomers.

In an attempt to develop alternative aqueous systems we had noticed that aqueous ceramic slurries dispersed using a mineral acid provide possibilities of using methylolurea monomers, the intermediates formed during preparation of urea-formaldehyde resins [5], for gel-forming. These monomers are inexpensive compared to acrylics and can be easily prepared. Since these monomers undergo polymerisation and cross-linking in acidic conditions they might be useful for gelcasting of ceramics such as alumina which could be dispersed in acidic medium. A procedure for preparation of highly concentrated (>55 vol%) aqueous alumina slurries, having viscosity less than 1 Pa s in acidic medium, as desired for gelcasting, has also been evolved by using a treatment of the particles with hydrolysed aluminium [6]. In this paper we report the results of our investigation on gelcasting of alumina using methylolurea monomers derived from urea and formaldehyde.

2. Experimental

The materials used in this investigation were A16SG alumina (Acc-Alcoa Ltd., India) and reagent grade urea and formaldehyde solution. Alumina was treated with hydrolysed aluminium for preparation of concentrated aqueous slurries as described in our previous paper [6].

Fig. 1 shows the flow chart of the gelcasting process. Premix solution was prepared by dissolving urea in formaldehyde solution at 1:4 mole ratio and aging the solution at ambient conditions for 24 h after adjusting the pH to 8.5 using dilute sodium hydroxide solution. The resulting solution was diluted with desired amount of water so as to prepare ~85 wt% alumina slurries containing organic part in the range 1.5 to 7.5 wt%.

Alumina slurries were prepared by mixing the powder in the premix solution at pH ~2.5 (acidified using dilute nitric acid) and stirring mechanically for about 30 min. Calculated amount of urea was added to the slurry at

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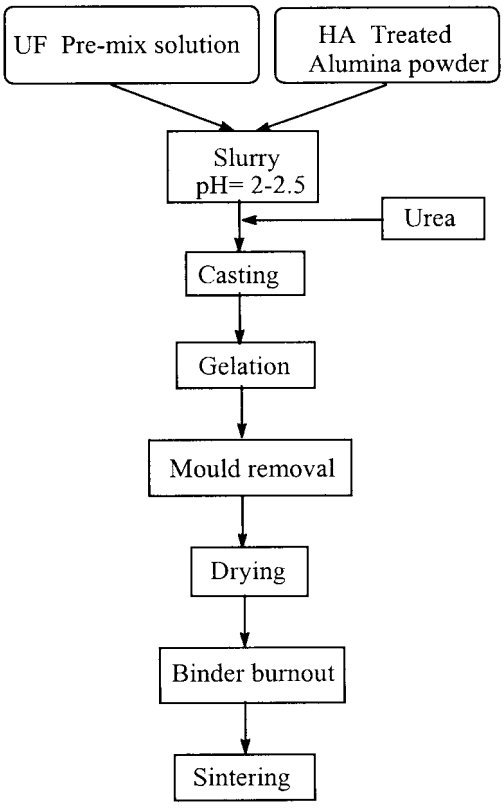

Fig. 1. Flowchart of gelcasting process.

the end of the process such that urea to formaldehyde mole ratio in the final composition was 1:2.

Gelation of the slurry was carried out at ambient conditions in wax (paraffin) molds. The gelled body which was removed from the mold by melting the wax was dried first in humidity controlled chambers to remove >95% of water and then in an air oven at 80°C.

The green bodies were debinderized in static air atmosphere, by ramping at a heating rate of 1°C/min from ambient to 350°C with hold at various temperatures in the range 150 to 250°C for different periods. The debinderized body was sintered at 1550°C for 2h by employing a heating rate of 5°C/min up to 600°C and 10°C/min from 600°C to the sintering temperature.

The apparent viscosity of the casting slip was measured in a Brookfield Synchrolectic viscometer (RVT/HBT model) using small volume adapter of coaxial geometry (SC4-13R). Green strength of the gelcast body was measured by diametrical compression test [7] using cylindrical specimens ($d=10$ mm, $h=4$ mm) in an Instron testing machine (model 1195) employing loading rate of 0.5 mm/min. Binder burnout profile of gelcast samples in air at dynamic and isothermal conditions were obtained by standard thermogravimetric analysis (Dupont Thermal Analyst 2000) and using a thermogravimetric apparatus constructed in the laboratory for analysis of large samples.

3. Results and discussion

3.1. Chemistry of premix solution

In alkaline solution urea combines with formaldehyde by successive replacement of amino hydrogens ($-NH_2$) with methylol group ($-CH_2OH$) to form methylolurea derivatives [5]. Thus a reaction mixture at equilibrium at temperature below 35°C will contain mono-, di- and trimethylolureas along with unreacted urea and formaldehyde at varying relative concentrations depending on the proportion of formaldehyde to urea. Upon acidification of this solution, condensation reactions continue between methylol group and free –NH–/–NH_2 hydrogens available in the system to form polymeric structures which causes gelation of the solution.

The solutions prepared using urea to formaldehyde at mole ratio higher than 1:4 were found unstable for use as premix solution due to precipitation of mono- and dimethylolureas on storing. The solutions containing urea and formaldehyde at mole ratio 1:4, on the other hand, was stable for weeks at pH 8.5 due to increase in relative concentration of highly soluble tri-methylolurea. However, due to the proportionate decrease in reactive amino and amido groups, further addition of urea was necessary to bring about gelation within a reasonable period suitable for gelcasting. Urea to formaldehyde mole ratio in the final composition was fixed at 1:2 since density maximum of the polymer was obtained at this composition.

When the premix solution supplemented with urea was acidified and allowed to stand, a turbidity appears first followed by gelation of the solution. The gelation time decreased with pH of the solution as shown in Fig. 2. A pH value between 2.5 and 3.0 at which gelation occurs within 30–80 min was selected for gelcasting.

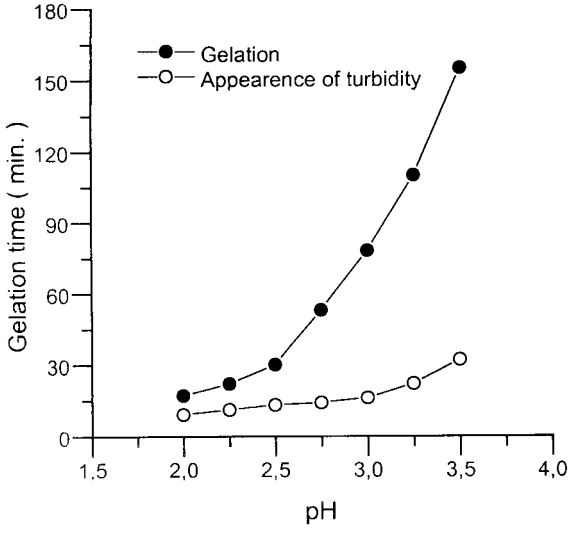

Fig. 2. Effect of pH on gelation time of premix solution.

3.2. Viscosity and flow of gelcasting slurry

Fig. 3 shows the viscosity of 55 vol% alumina slurry at pH 2.5 containing the urea-formaldehyde (UF) monomers 6% by weight of alumina. The slurry exhibited shear thinning behaviour with a viscosity value ~500 mPa s at 9.3 s^{-1} which decreased to ~170 mPa s at 93 s^{-1}. The viscosity values, particularly at low shear rates, was found significantly lower than observed for its counterpart without UF monomers indicating that interactions of UF with alumina surfaces impart semisteric stabilization of the slurry. It has been reported that UF chemically interacts with alumina surfaces (hydrolysed aluminium) through amido nitrogen [8]. Appreciable change in viscosity was not observed on keeping the slurry over 1 h which provides sufficient working time for dispersion of alumina in the premix solution. Significant increase in viscosity was, however, observed after a period corresponding to the appearance of turbidity on supplementing the slurry with urea.

3.3. Molding and drying

Since gelation takes place at temperatures <35°C a wax (paraffin) mold could be used for gelcasting and the gelled body could be removed immediately after gelation by melting the mold away. When gelation was carried out in glass or plastic molds partial drying of the gelled body in the mold was desirable to remove the body without any deformation.

Drying of gelled body is generally carried out in humidity controlled chambers since rapid drying can cause warpage or cracking due to non-uniform shrinkage [9]. In the present case drying was accomplished by employing relative humidity of 90, 80 and 65% successively at room temperature to moisture content less than 5% and then keeping in an air oven at 80°C for 24 h.

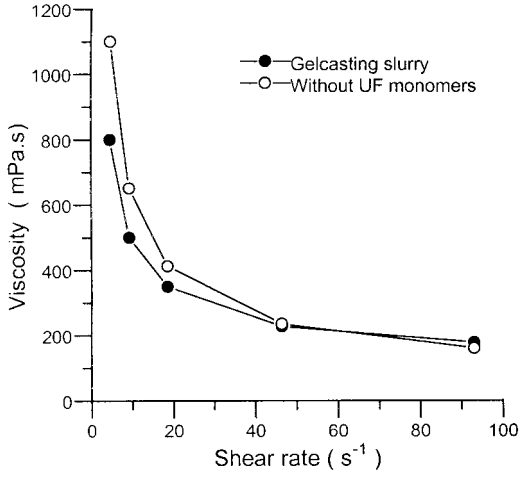

Fig. 3. Viscosity versus shear rate of gelcasting slurry containing 55 vol% alumina.

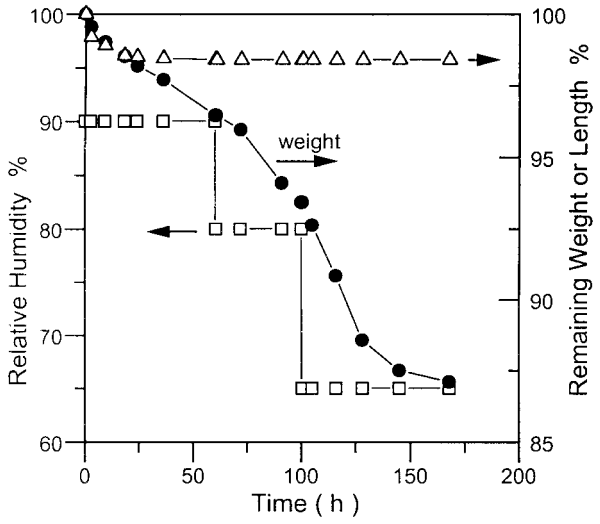

Fig. 4. Drying profile of gelled body at room temperature under humidity controlled conditions.

Fig. 4 shows a typical humidity controlled drying profile of a cylindrical specimen of size 2.5×3.0 cm. The average linear shrinkage observed after drying was 1.6%.

3.4. Green density and strength

Fig. 5 shows the variation in density (corrected for organic content) and green strength of dried bodies with polymer content. Density did not show any appreciable change with increase in the binder content upto 6 wt%, but linearly decreased with further increase in the binder content. Green strength, on the other hand, showed a significant increase with binder content upto 6 wt% and then marginally upto 10 wt%. The results show that optimum properties of the green body with respect to powder compaction and strength are obtained at a binder content ~6 wt% at which the density and strength

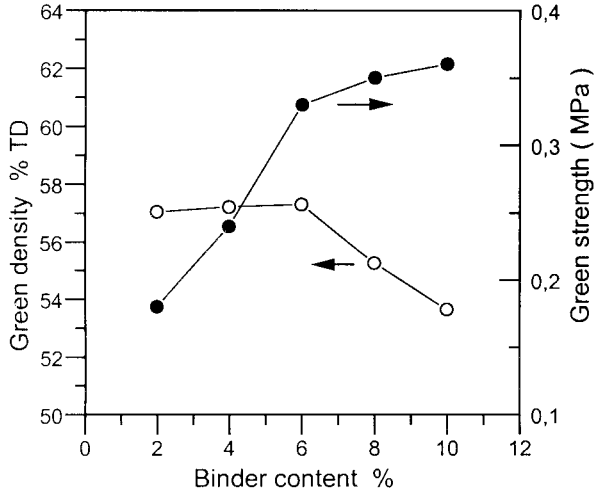

Fig. 5. Effect of polymer content on green density (corrected for organic content) and green strength.

measured were approximately 57% (TD) and 0.35 MPa, respectively.

3.5. Binder burnout and sintering

Fig. 6 shows the binder burnout profile of gelcast sample containing 6 wt% binder in comparison with neat UF polymer obtained by conventional thermogravimetric analysis (TGA) in air at 10°C/min. It can be seen that UF in presence of alumina decomposes completely in two steps at temperature below 350°C, whereas neat UF decomposes in three steps extending upto 610°C. Since the last step of degradation of neat UF corresponds to fragmentation of more thermally stable structures formed in the previous step [10], the early decomposition of UF in presence of alumina may be attributed to retardation of these reactions induced by chemical interaction of UF with alumina surfaces (hydrolysed aluminum) [8]. This would enable binder burnout in a shorter period in the present case than possible using acrylic binders which needs heating upto 560–650°C for complete burnout [2].

Binder burnout is generally carried out at dynamic conditions employing a heating rate as low as 10–60°C/h in order to attain a slow and steady state binder burnout profile. However, thermograms of the present system at isothermal conditions (Fig. 7) indicate that burnout of bulk of the binder at slow and steady state can also be achieved by holding the samples at 150, 160, 170, 180/190 and 200°C for different periods. Fig. 8 shows the binder burnout profile of a typical large cylindrical body (2.5×3.0 cm) obtained by ramping from 80 to 350°C at 60°C/h with hold at above mentioned temperatures. A linear shrinkage less than 0.3 % was observed on removal of the binder.

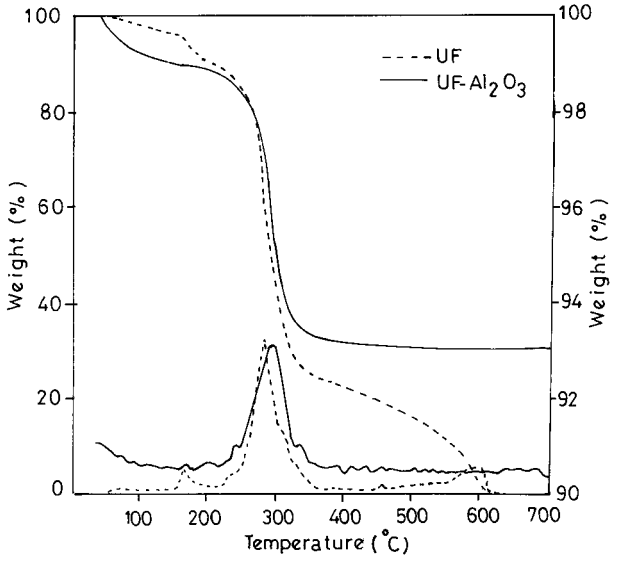

Fig. 6. TGA of gelcast sample in comparison with neat UF polymer.

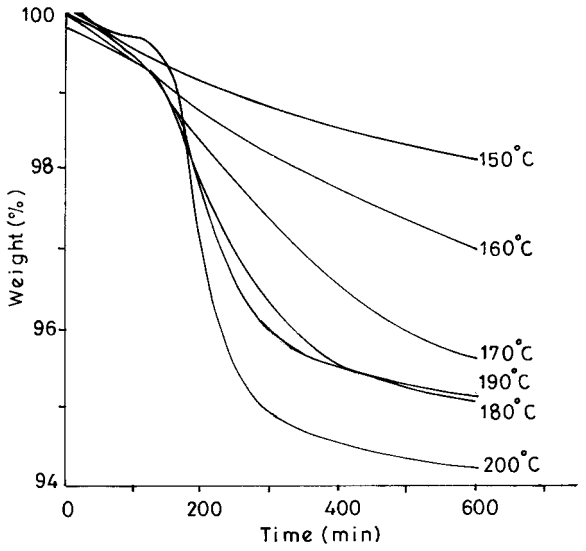

Fig. 7. Isothermal TGA of gelcast samples at various temperatures.

It has been reported that bulk of the pyrolytic products of UF polymer constitute low molecular weight species such as H_2O, CO_2, CH_2O and NH_3 [10]. Therefore, employment of a higher rate of binder burnout than used in this study may be possible since pyrolytic products of low molecular dimensions can pass through narrow channels available in the particle assembly without disrupting the particle arrangement and creating defects.

The debinderized body upon sintering at 1550°C showed a density ~97% of theoretical density. The shrinkage during sintering was isotropic and averaged 14 to 16%. Fig. 9 shows a spur gear of alumina obtained by using the present method.

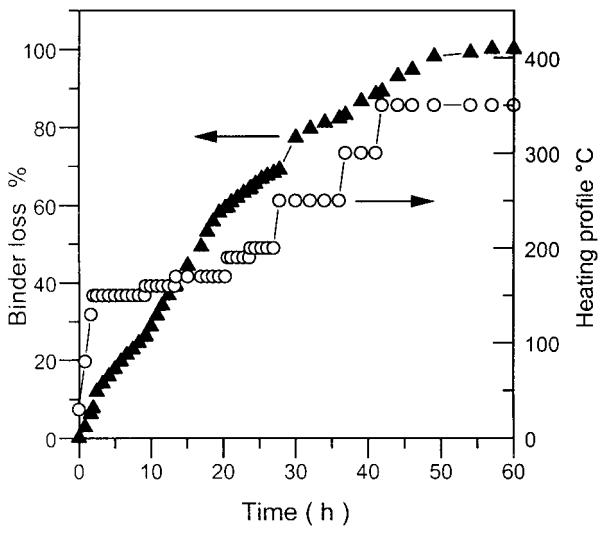

Fig. 8. Binder burnout profile of large cylindrical body ($D=2.5$ cm, $H=3$ cm).

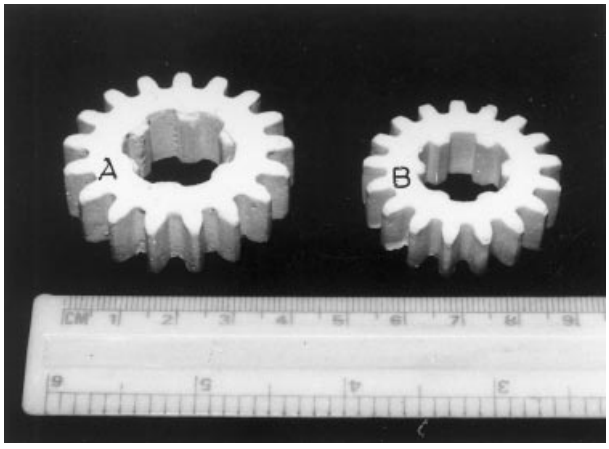

Fig. 9. A spur gear of alumina, (A) green and (B) sintered, prepared by gelcasting using urea-formaldehyde.

4. Conclusions

A new aqueous gelcasting system for alumina was evolved using concentrated (55 vol%) scurries dispersed at pH 2.5–3 using nitric acid. Gelation of the slurry was accomplished at ambient conditions during 30–80 min by in-situ polymerisation of methylolurea monomers derived from urea and formaldehyde. Green bodies prepared using a typical alumina of average particle size of 0.34 μm showed a density maximum (corrected for organic content) of 57% TD and strength of 0.35 MPa at polymer content about 6% by weight of alumina. Debinderization of the green body was accomplished by pyrolysis in air below 350°C. The density of the body sintered at 1550°C for 2 h was 97% TD and the shrinkage during sintering was isotropic and averaged 14 to 16%.

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