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# A new direct coagulation casting process for alumina slurries prepared using poly(acrylate) dispersant

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## Abstract

Direct coagulation casting (DCC) of concentrated aqueous alumina slurries prepared using ammonium poly(acrylate) dispersant has been studied using MgO as coagulating agent. Addition of small amounts of MgO increased the viscosity of the concentrated alumina slurries with time and finally transformed it in to a stiff gel. Sufficient working time for degassing and casting could be achieved by cooling the slurries to a temperature of ~5 °C after proper homogenization after the addition of MgO. The DCC slip with alumina loading in the range of 50–55 vol% showed relatively low viscosity (0.12–0.36 Pa s at shear rate of 93 $s^{-1}$) and yield stress (1.96–10.56 Pa) values. The wet coagulated bodies prepared from slurries of alumina loading in the range of 50–55 vol% had enough compressive strength (45–211 kPa) for handling during mould removal and further drying. The coagulated bodies prepared from slurries of alumina loading in the range of 50–55 vol% showed linear shrinkage in the range of 4.8–2.3 during drying and 17.1–16.2 during sintering respectively. Near-net-shape alumina components with density >98% TD could be prepared by the DCC process.

*Keywords:* A. Suspensions; A. Shaping; D. $Al_2O_3$; D. MgO; Direct coagulation casting

## 1. Introduction

Near-net-shape fabrication by gelation of concentrated aqueous ceramic powder suspensions cast in a mould is an easy and cost effective method for fabrication of ceramic components [1–4]. Gelcasting and direct coagulation casting (DCC) are well-established methods for fabrication of near-net-shape components from concentrated ceramic powder suspensions by the gelation approach. In gelcasting, in situ polymerization of organic monomers and cross-linking agents added in the suspensions are used to immobilize the particles in a suspension and thereby set the slurry in to a strong gel [5–9]. In DCC, gelation of the ceramic powder suspensions in a mould is carried out by coagulation by shifting the force between the particles in the suspension from the repulsive to the attractive regime [10–29]. The force between the particles is shifted from the repulsive to the attractive regime either by shifting the pH of the suspension towards its isoelectric point by time-delayed in situ generation of an acid or a base or by compressing the electrical double layer by in situ generation of excess electrolytes [10–29].

Gauckler and co-workers pioneered the DCC of ceramic powder suspensions by in situ generation of ammonia by enzyme (urease) catalyzed hydrolysis of urea [10–20]. In this, either the ammonia generated by in situ hydrolysis of the urea increases the pH of the suspensions, prepared in acidic range only by pH adjustment, towards its isoelectric point or the ammonium bicarbonate and ammonium carbonate produced from $CO_2$ and ammonia generated from the urea hydrolysis compress the electrical double layer in suspensions prepared in alkaline pH using dispersants [10–20]. Direct coagulation casting of concentrated ceramic powder suspensions prepared in alkaline pH range using polyelectrolyte dispersants has been carried out by in situ generation of acids either by hydrolysis of compounds such as acid anhydrides, esters and lactones or thermal decomposition of hydroxyl aluminium di-acetate added in the slurry [21–28].

Recently we have reported a novel coagulation method for aqueous alumina slurries prepared using ammonium poly(acrylate) dispersant [29–30]. In this, time dependent in

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situ generation of $Mg^{2+}$ ions from sparingly soluble MgO has been used to coagulate the suspension in to a stiff gel. The reactions leading to coagulation of the alumina suspension are as shown below

$$\text{Ammonium poly (acrylate)}_{\text{(Aqueous)}} \rightleftarrows \text{Ammonium poly (acrylate)}_{\text{(Adsorbed on alumina)}}$$

$$MgO + H_2O \rightleftarrows Mg^{2+} + 2OH^-$$

$$\text{Ammonium poly (acrylate)}_{\text{(Aqueous)}} + Mg^{2+} \rightarrow \text{Mg-poly (acrylate)} + NH_4{}^+$$

The $Mg^{2+}$ ions react with the un-adsorbed ammonium poly(acrylate) in the dispersion medium and form precipitate of Mg-poly(acrylate). This resulted in desorption of ammonium poly(acrylate) from the alumina surface. The desorption of ammonium poly(acrylate) from the alumina particle surface leads to insufficient dispersant surface coverage and hence coagulation of the suspension. The present work reports DCC using the novel coagulation method for near-net-shape fabrication.

## 2. Experimental

A16SG alumina powder (ACC Alcoa, India) of average particle size 0.34 μm (measured using Malvern Master Size Analyzer 2000, UK) and surface area 10.4 $m^2/g$ (measured using surface area analyzer, Sorptomatic 1990, Thermo Fennigan, Italy) was used. A 35 wt.% aqueous solution of ammonium poly(acrylate) was used as the dispersing agent. Analytical reagent grade light MgO powder (Thomas Baker, Mumbai) of surface area 32.1 $m^2/g$ was used as coagulating agent. Distilled water was used for preparation of slurries.

The flowchart of the direct coagulation casting process is shown in Fig. 1. Alumina slurries were prepared by tumbling the alumina powder, water and various amount of the dispersing agent in polyethylene containers along with zirconia grinding media for 12 h. 0.2 wt.% MgO powder based on alumina was added to the slurries and mixed thoroughly by continuing the tumbling process for another 30 min. The slurries cast in cylindrical moulds were allowed to gel either at room temperature or by heating at 70 °C in an oven. The slurries gelled at 70 °C were removed from the mould after cooling to the room temperature. The gelled bodies removed from the mould were dried at room temperature (30 °C) at a relative humidity of ~75. The humidity condition was created in a desiccator using saturated sodium chloride solution. The bodies dried under the humidity conditions were further dried in air at room temperature. The drying shrinkage and green density of the alumina bodies was calculated from dimensional measurements. The green bodies were sintered at 1600 °C for 2 h. Heating rate used for sintering was 2 °C/min up to 300 °C and then 5 °C/min up to 1600 °C. Density of the sintered samples was measured by Archimedes principle. Microstructure of the green and sintered samples was observed on fractured surface using a scanning electron microscope (LEO 1455).

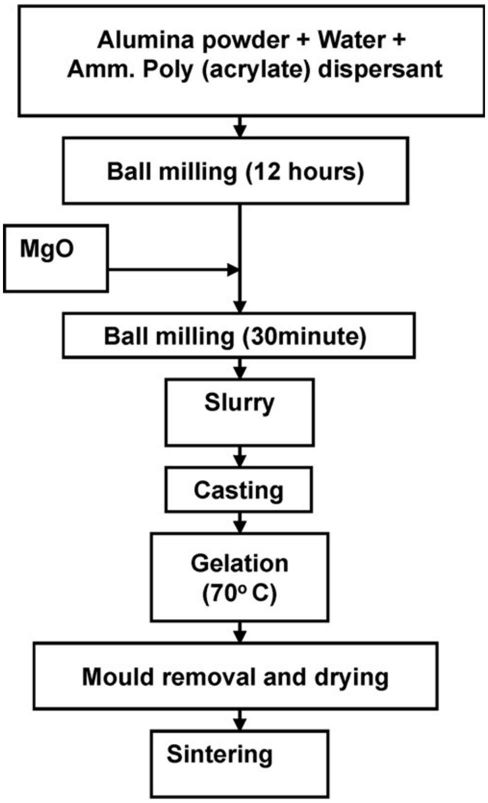

Fig. 1. Flowchart of the direct coagulation casting process.

The viscosity of the slurries was measured using Brookfield viscometer (RVT model) using small sample adapter and cylindrical spindles (SC 21 and SC 28). The viscosity of the slurries at various temperatures was measured using a thermo cell assembly along with the Brookfield viscometer. The yield stress value of the slurries is calculated by graphical method using Casson model [31].

The compressive stress–strain behavior of the wet coagulated bodies was measured using a universal testing machine (Hounsfield, S-sires, UK) at a cross-head speed of 2 mm/min. Cylindrical coagulated bodies of 22 mm diameter and 45 mm length used for compressive strength measurement were prepared by gelling slurries of alumina loading in the range 50–55 vol% in closed stainless steel moulds. The gelation of the slurries was carried out by heating at 70 °C for 20 min. The gelled bodies were aged overnight and removed from the mould immediately before the testing. The compressive strength (defined as the yield stress) and bulk modulus of the gels was determined from the stress–strain graph [16].

## 3. Results and discussion

Fig. 2 shows viscosity of the 50 vol% aqueous alumina powder suspensions containing various amount of the dispersing agent. The slurry showed minimum viscosity of 0.25 Pa s at 0.43 wt.% of the dispersing agent. The viscosity of the slurry increased marginally with further addition of the dispersing agent and reached a value of 0.5 Pa s at 1.04 wt.% of the dispersing agent. This indicates that well-dispersed suspension

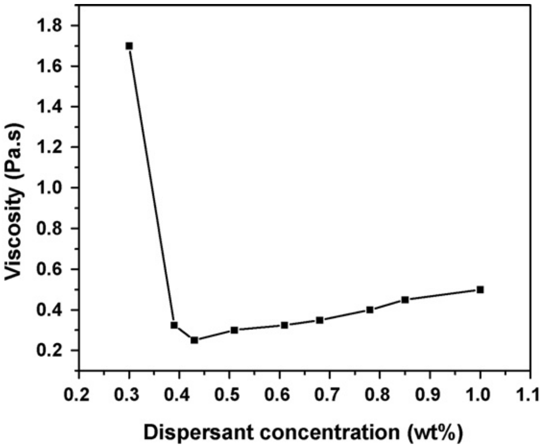

Fig. 2. Viscosity versus dispersant concentration of 50 vol% alumina slurry.

of the alumina powder could be prepared at a minimum dispersant concentration of 0.43 wt.% and addition of higher amount of dispersant (up to ~1 wt.%) did not affect much the dispersion of the powder [32–33].

It has been reported in our previous publication that DCC using MgO is possible at dispersant concentration much higher than that required for optimum dispersion of the powder [29]. The slurries prepared at dispersant concentration of below 0.84 wt.% underwent premature coagulation at room temperature (30 °C) up on the addition of MgO and found not suitable for DCC at room temperature [29]. Though DCC of the slurries prepared at dispersant concentration below 0.84 wt.% could be performed by cooling the slurry to a temperature of ~5 °C before mixing with MgO, the gelled bodies prepared from them needs to be handled carefully to avoid deformation during mould removal and drying due to their low strength. Therefore, slurries prepared at 0.84 wt.% dispersant concentration are used for DCC in the present work. Fig. 3 shows effect of addition of 0.2 wt.% MgO on the viscosity of 50 vol% alumina slurry prepared at dispersant concentration of 0.84 wt.%. The slurry showed a slight increase in viscosity from 0. 25 to 2.5 Pa s during the initial five minutes after the addition MgO due to heterocoagulation of alumina particles having negative surface charge and MgO particles having positive surface charge at the processing pH (~9.2) [29,34]. However, viscosity of the slurry decreased with further milling and reached a value of 0.6 Pa s in 35 min. That is, viscosity of the slurry reached near to the value before addition of MgO in 35 min. During milling, the agglomerates formed by heterocoagulation break down and the MgO particles co-disperse with alumina due to excess ammonium poly(acrylate) present in the dispersion medium. After reaching the minimum value, viscosity of the slurry slowly increased with time for another 30 min and then increased rapidly. It is worthy to note that the slurry viscosity remains in the castable range (1–1.5 Pa s) for 20 min after reaching the minimum value and reached a gel-like consistency (viscosity above 40 Pa s) in 250 min after the addition of MgO. That is, casting of the slurry at room temperature could be performed with in 20 min after homogenizing the MgO in the alumina slurry by ball milling for 35 min. Further, the slurry cast in closed cylindrical mould could be removed without deformation after aging for 5 h at room temperature.

In an ideal DCC process the viscosity of the slurry should remain unchanged for a sufficient period of time after addition the coagulating agent to facilitate the degassing and casting operations [18,26]. Though the viscosity of the slurry is in the castable range for 20 min at room temperature (~30 °C) during which the degassing and casting can be performed, the viscosity of the slurry could be maintained low for longer period of time by cooling to a temperature of ~5 °C by keeping in an ice bath, for comfortable working time before casting. Fig. 4 shows viscosity variation of the slurry with time at temperature of ~5 °C. The slurry was cooled after 35 min of ball milling after the addition of MgO. The viscosity of the slurry decreased from 0.6 to 0.35 Pa s within 10 min during cooling. This viscosity value is very close to the viscosity of the slurry before the addition MgO. Further, the viscosity of the slurry remains more or less constant over a period of 3 h. This is because of decrease in the rate of reactions leading to the coagulation of the slurry due to lower solubility of MgO at

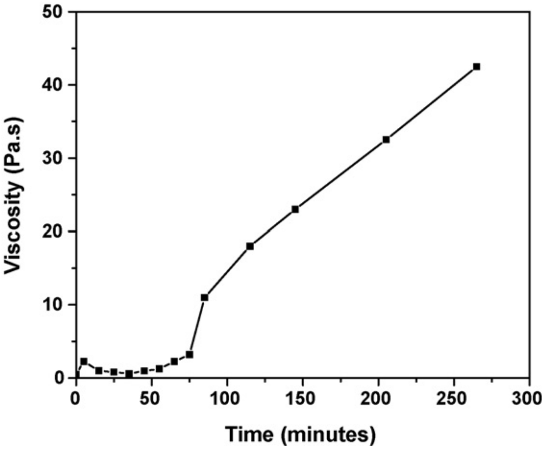

Fig. 3. Effect of addition of 0.2 wt.% MgO on alumina slurries containing 0.84 wt.% of the dispersing agent.

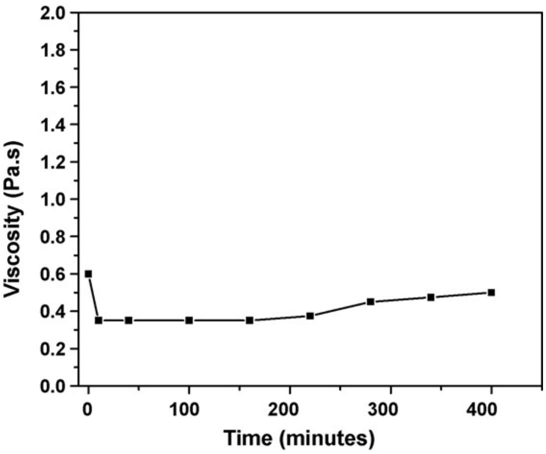

Fig. 4. Effect of cooling on the viscosity variation with time of 50 vol% alumina slurry prepared at 0.84 wt.% dispersant added with 0.2 wt.% MgO. (The slurry was cooled after 35 min of ball milling at room temperature after the addition of MgO.)

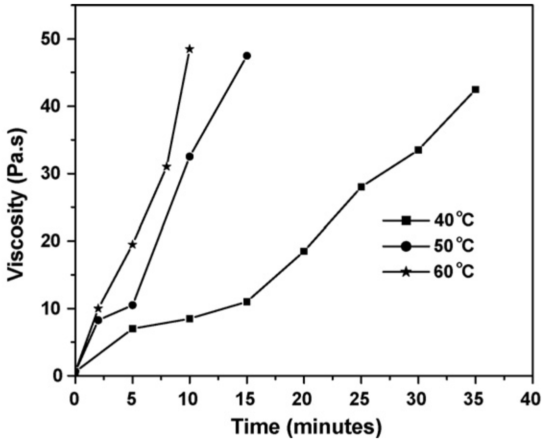

Fig. 5. Effect of temperature on viscosity of 50 vol% alumina slurry prepared at 0.84 wt.% dispersant and added with 0.2 wt.%MgO. (The slurry was heated after 35 min of ball milling at room temperature after the addition of MgO.)

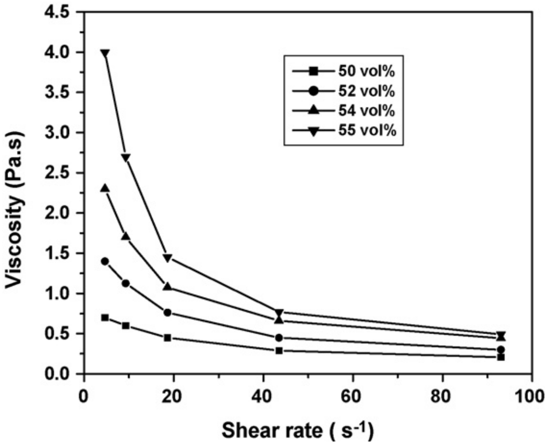

Fig. 6. Viscosity versus shear rate plot of DCC slurries of various alumina loading at room temperature (~30 °C).

low temperature. It is well known that the rate of adsorption increases with decrease of temperature. On cooling, the excess dispersant molecules in the dispersion medium easily adsorb on the MgO particle surface and disperse them well along with alumina particles resulted in decrease of viscosity. On the other hand, at room temperature (30 °C), the reactions being fast, coagulation by depletion of dispersant from alumina particle surface begins before all the agglomerates formed by hetero-coagulation re-disperse. Therefore, the slurry viscosity started increasing before reaching the value before addition of MgO at room temperature.

It is well known that usefulness of any ceramic forming process depend on its production rate. For successful commercialization, the process should have high or moderate production rate. However, in the present process, the slurry cast in cylindrical mould needs nearly 5 h aging for forming a stiff gelled body that could be removed without deformation. That is production rate at room temperature is relatively low. However, the viscosity of the slurries could be increased rapidly by increasing the temperature. Fig. 5 shows effect of temperature on the viscosity of 50 vol% alumina slurry prepared at 0.84 wt.% dispersant added with 0.2 wt.% of MgO. The measurements were started after 35 min of ball milling after the addition of MgO at which the slurry viscosity reaches minimum value. The slurry heated at temperature in the range of 40–60 °C form gel-like consistency at time period in the range of 35–10 min. The slurry cast in closed mould becomes stiff gel during heating in an oven at 70 °C for 20 min. The gelled body could be removed from the mould without any deformation immediately after cooling to room temperature.

Fig. 6 shows viscosity at various shear rates of DCC slurries of alumina loading in the range of 50–55 vol% containing 0.84 wt.% of the dispersing agent and 0.2 wt.% of MgO at room temperature. The viscosity measurements were taken after 35 min of ball milling after the addition of MgO. All the slurries showed pseudoplastic flow behavior. As expected, both viscosity and pseudoplastic behaviors of the slurries increased with solids loadings. The slurry with solids loading up to 55 vol% showed flow property suitable for casting. The slurries having alumina loading in the range of 50–55 vol% showed a viscosity of 0.205–0.49 Pa s respectively at shear rate of 93 $s^{-1}$. However, corresponding viscosity values at lower shear rate of 4.65 $s^{-1}$ is in the range of 0.7–4 Pa s. Yield stress of the slurries provides a direct insight in to the pourability of the suspensions. The yield stress, the shear stress required to induce flow, determined by graphical method using Casson model, for the casting slip of solids loading in the range of 50–55 vol% is in the range of 2.25–12.6 Pa respectively. The slurries having yield stress value in this range could be easily poured in to a mould for making near-net-shape components. Considerable decrease in viscosity and yield stress values of the DCC slurries could be achieved by cooling the slurries in an ice bath after homogenization for 35 min by ball milling after the addition of MgO. The slurries of alumina loading in the range of 50–55 vol% cooled in ice bath showed viscosity in the range of 0.12–0.36 Pa s at shear rate of 93 $s^{-1}$. The corresponding viscosity values at lower shear rate of 4.65 $s^{-1}$ is in the range of 0.55–2.9 Pa s. The yield stress values of the slurries cooled at a temperature of ~5 °C calculated using casson model are in the range of 1.96–10.56 Pa respectively. Fig. 7 shows viscosity at

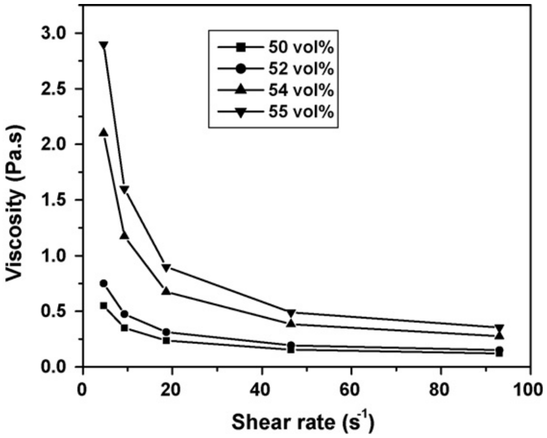

Fig. 7. Viscosity versus shear rate plot of DCC slurries of various alumina loading at temperature of ~5 °C. (The slurry was cooled after ball milling for 35 min after the addition of MgO.)

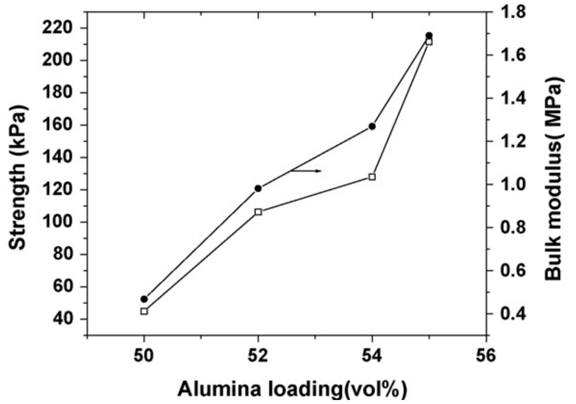

Fig. 8. Compressive strength and modulus of wet coagulated bodies prepared by the direct coagulation casting from slurries of various alumina loading.

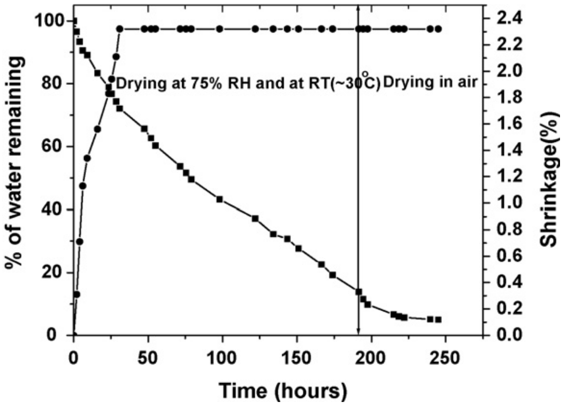

Fig. 9. Drying characteristics of the coagulated body (prepared from slurry of alumina loading 55 vol%).

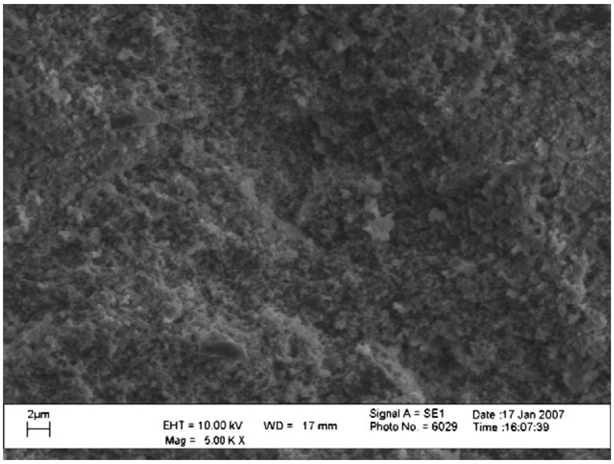

Fig. 10. SEM photograph of fractured surface of alumina green body prepared by the direct coagulation casting process.

various shear rates of DCC slurries of alumina loading in the range of 50–55 vol% cooled in an ice bath after homogenization after the addition of MgO.

In a DCC process the wet coagulated bodies should have sufficient strength for easy handling during further processing such as mould removal and drying. Fig. 8 shows compressive strength and bulk modulus of wet coagulated bodies (gels) prepared from slurries of alumina loading in the range 50–55 vol%. The compressive strength and bulk modulus values increased with alumina loading. The wet coagulated bodies with alumina loading in the range of 50–55 vol% showed a compressive strength in the range of 45–211 kPa respectively. The corresponding modulus values observed is in the range of 0.468–1.690 MPa respectively. This much gel strength is enough for handling of the gels during mould removal and drying. No deformation or sagging was observed during mould removal and drying.

In order to avoid warpage and crack, the coagulated bodies were dried at 75% relative humidity at room temperature (~30 °C) [35]. Fig. 9 shows drying characteristics of the gels prepared from DCC slurry of 55 vol% alumina loading. The body showed a faster drying rate in the first 24 h. Majority of the drying shrinkage takes place during this period and shrinkage of the body apparently stops at the end of 30 h. After 24 h, drying rate was more or less steady for period of nearly 190 h. Nearly 86% of water present in the coagulated body was removed at 190 h. After this, the body was dried in air atmosphere at same temperature for another 48 h. Air-drying for 48 h leave nearly 5% of total water in the green body and that was removed by further drying at 120 °C.

Drying shrinkage of the gelled bodies decreased and density of the green bodies increased with increase in solids loading of the slurry. The linear drying shrinkage observed for the gelled bodies prepared from slurries of solids loading in the range of 50–55 vol% was in the range of 4.8–2.3%. The corresponding green density observed was in the range of 55.4–58.4% of theoretical density of alumina. SEM photograph of fractured surface of the alumina green body prepared by the coagulation casting process showed uniform microstructure. Fig. 10 shows SEM photograph of fractured surface of the green alumina body.

A slight increase in sintered density and decrease in linear sintering shrinkage was observed with increase in solids loading of the alumina slurry. The sintered density observed was in the range of 97.2–98.5% theoretical value and the corresponding linear shrinkage was in the range of 17.1–16.2%. The characteristics of the alumina bodies prepared by the direct coagulation casting process are shown in Table 1. Fig. 11 shows SEM photograph of the fractured surface of sintered alumina

Table 1
Characteristics of the alumina bodies prepared by the direct coagulation casting process

| Slurry solid loading (vol%) | Linear drying shrinkage (%) | Green density (%TD) | Linear sintering shrinkage (%) | Sintered density (%TD) |
|---|---|---|---|---|
| 50 | 4.8 | 55.4 | 17.1 | 97.2 |
| 52 | 4.0 | 55.6 | 16.5 | 97.9 |
| 54 | 3.2 | 57.1 | 16.3 | 97.9 |
| 55 | 2.3 | 58.4 | 16.2 | 98.5 |

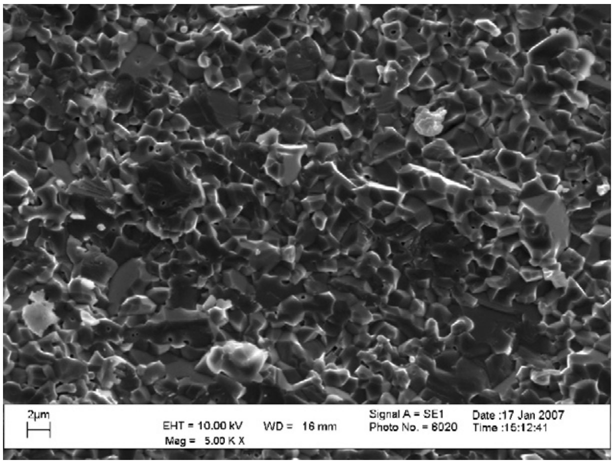

Fig. 11. SEM photograph of fractured surface of sintered alumina ceramics prepared by the direct coagulation casting process.

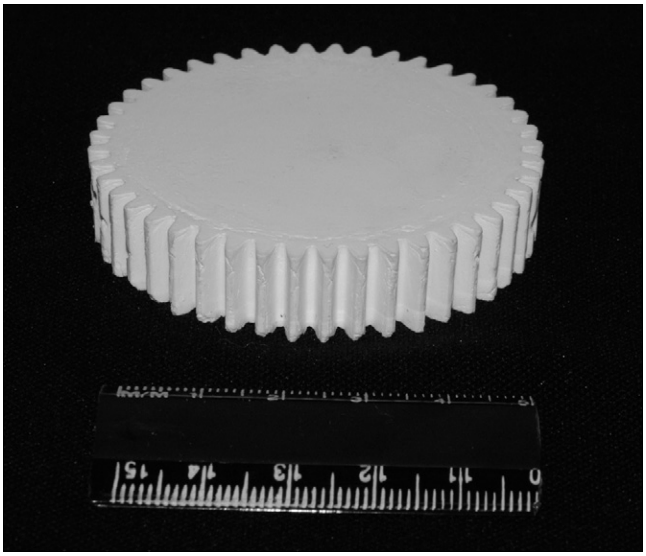

Fig. 12. Photograph of sintered alumina spur gear fabricated by the direct coagulation casting.

ceramics prepared by the direct coagulation casting process. Only few micro pores were observed within the alumina grains. The average grain size calculated from the microstructure by linear intercept method was 2.6 μm.

The new direct coagulation process could fabricate near-net-shape bodies. Fig. 12 shows photograph of a sintered alumina spur gear fabricated by the direct coagulation casting process. The slurry set in the mould by coagulation at room temperature (∼30 °C) was removed from the mould after overnight aging to avoid any deformation. However, the slurry coagulated in the mould by keeping in an oven at 70 °C for 20 min could be removed without any deformation immediately after cooling the mould to room temperature.

## 4. Conclusions

Direct coagulation casting of concentrated aqueous alumina powder suspensions prepared using ammonium poly(acrylate) dispersant has been studied using MgO as coagulating agent. Cooling the slurry after proper homogenization after the addition of MgO provides sufficient time (<3 h) for carrying out degassing and casting operations. The DCC slip with alumina loading in the range of 50–55 vol% showed low viscosity (0.12–0.36 Pa s at shear rate 9.3 $s^{-1}$) and yield stress (1.96–10.56 Pa) values. The wet coagulated bodies prepared from slurries of alumina loading in the range of 50–55 vol% have enough strength (45–211 kPa) for handling during mould removal and further drying. The coagulated bodies prepared from slurries of alumina loading in the range of 50–55 vol% showed linear shrinkage in the range of 4.8–2.3% during drying and 17.1–16.2% during sintering respectively. The green bodies prepared by the DCC process achieved a density of >98% TD by sintering at 1600 °C for 2 h. Near-net-shape components could be fabricated by the direct coagulation process.

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## References

[1] H.M. Wyss, E.V. Tervoort, L.J. Gauckler, Mechanics and microstructure of concentrated gels, J. Am. Ceram. Soc. 88 (2005) 2337–2348.
[2] W.M. Sigmund, N.S. Bell, L. Bergstrom, Novel powder processing methods for advanced ceramics, J. Am. Ceram. Soc. 83 (2000) 1557–1574.
[3] F.F. Lange, Powder processing science and technology, J. Am. Ceram. Soc. 72 (1989) 3–15.
[4] J.A. Lewis, Colloidal processing of ceramics, J. Am. Ceram. Soc. 83 (2000) 2341–2359.
[5] O.O. Omatete, M.A. Janney, R.A. Strelow, Gelcasting—a new ceramic forming process, Am. Ceram. Soc. Bull. 70 (1991) 1641–1647.
[6] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Menchofer, Gelcasting of alumina, J. Am. Ceram. Soc. 81 (1998) 581–591.
[7] M. Takahashi, H. Unuma, Gelcasting, Ceram. Jpn. 32 (1997) 102–105.
[8] M.A. Janney, O.O. Omatete, C.A. Walls, S.D. Nunn, R.J. Ogle, Development of low toxicity gelcasting system, J. Am. Ceram. Soc. 81 (1998) 581–591.
[9] K. Prabhakaran, C. Pavithran, Gelcasting of alumina using urea formaldehyde. II: Gelation and ceramic forming, Ceram. Int. 26 (2000) 67–71.
[10] F.H. Baader, T.J. Graule, L.J. Gauckler, Direct coagulation casting—a new green shaping technique. Part I: Application to alumina, Ind. Ceram. 16 (1996) 31–36.
[11] F.H. Baader, T.J. Graule, L.J. Gauckler, Direct coagulation casting—a new green shaping technique. Part II: Application to alumina, Ind. Ceram. 16 (1996) 36–40.
[12] J.A. Gauckler, T.J. Graule, F. Baader, Ceramic forming using enzyme catalyzed reactions, Mater. Chem. Phys. 61 (1999) 78–102.
[13] B. Balzer, M.K.M. Hruschka, L.J. Gauckler, In situ rheological investigation of the coagulation in aqueous alumina suspensions, J. Am. Ceram. Soc. 84 (2001) 1733–1739.
[14] B. Blazer, M.K.M. Hruschka, L.J. Gauckler, Coagulation kinetics and mechanical behaviour of wet alumina green bodies produced via DCC, J. Colloid Interface Sci. 216 (1999) 379–386.
[15] L.J. Gauckler, T.J. Graule, F. Bader, J. Will, Enzyme catalysis of alumina foaming, Key Eng. Mater. 159–160 (1999) 130–150.
[16] D. Hesselbarth, E. Tervoort, C. Urban, L.J. Gauckler, Mechanical properties of coagulated wet particle net works with alkali swellable thickners, J. Am. Ceram. Soc. 84 (2001) 1689–1695.

[17] A.R. Studart, C.V. Pandolfelli, E. Tervoort, L.J. Gauckler, In situ coagulation of high alumina zero cement refractory castables, J. Am. Ceram. Soc. 85 (2002) 1947–1953.

[18] B. Balzer, L.J. Gauckler, Novel colloidal forming techniques: direct coagulation casting, in: S. Somiaya (Ed.), Hand Book of Advanced Ceramics, vol. I, Material Science, Elsevier Academic Press, London, 2003, pp. 453–458.

[19] W. Si, T.J. Graule, F.H. Baader, L.J. Gauckler, Direct coagulation casting of silicon carbide components, J. Am. Ceram. Soc. 82 (1999) 1129–1136.

[20] M.K.M. Hruschka, W. Si, S. Tosatti, T.J. Graule, L.J. Gauckler, Processing of $\beta$-silicon nitride from water based $\alpha$-silicon nitride, alumina and yttria powder suspensions, J. Am. Ceram. Soc. 82 (1999) 2039–2043.

[21] K. Prabhakaran, S. Ananthakumar, C. Pavithran, Preparation of extrudable alumina paste by coagulation of electrosterically stabilized aqueous slurries, J. Eur. Ceram. Soc. 22 (2002) 153–158.

[22] A.L. Penard, F. Rossignol, H.S. Nagaraja, C. Pagnoux, T. Chartier, Dispersion of $\alpha$-alumina ultrafine powders using 2-phosphonobutane 1,2,3 tricarboxylic acids for the implementation of a DCC, J. Eur. Ceram. Soc. 25 (2005) 1109–1118.

[23] A.L. Penard, F. Rossignol, C. Pagnoux, T. Chartier, C. Cueille, M.E. Murphy, Coagulation of concentrated suspension of ultra fine alumina powders by PH Shift, J. Am. Ceram. Soc. 89 (2006) 2073–2079.

[24] R. Laucournet, C.T. Pagnoux, C. Chartier, J.F. Baumard, Coagulation method of aqueous concentrated alumina suspensions by thermal decomposition of hydroxyl aluminium diacetate, J. Am. Ceram. Soc. 83 (2000) 2661–2667.

[25] Y. Yin, J.G.P. Binner, M.J. Hey, J.R. Mitchell, Hydrolysis of carboxylic lactones in alumina slurries, J. Eur. Ceram. Soc. 26 (2006) 1171–1177.

[26] J.G.P. Binner, I. Santacruz, A.M. Mc Dermott, Rheological characterization of electrosterically dispersed alumina suspensions during in situ coagulation, J. Am. Ceram. Soc. 89 (2006) 863–868.

[27] J.G.P. Binner, A.M. Mc dermott, Y. Yin, R.M. Sambrook, B. Vaidhyanathan, In situ coagulation moulding: a new route for high quality net shape ceramics, Ceram. Int. 32 (2006) 29–35.

[28] R. Laucournet, C. Pagnoux, T. Chartier, J.F. Baumard, Coagulation method of aqueous concentrated alumina suspensions by thermal decomposition of hydroxyl aluminium diacetate, J. Am. Ceram. Soc. 83 (2000) 2661–2667.

[29] K. Prabhakaran, R. Sooraj, A. Melkeri, N.M. Gokhale, S.C. Sharma, Novel coagulation method for direct coagulation casting of aqueous alumina slurries prepared using poly (acrylate) dispersant, J. Am. Ceram. Soc. 91 (2008) 615–619.

[30] K. Prabhakaran, A. Melkeri, N.M. Gokhale, S.C. Sharma, Process of producing ceramic articles by depletion coagulation, Indian Patent File No. 1312/DEL/2007.

[31] J.C. Chang, F.F. Lange, D.S. Pearson, Viscosity and yield stress of alumina slurries containing large concentration of electrolyte, J. Am. Ceram. Soc. 77 (1994) 19–26.

[32] J. Cesarano III, I.A. Aksay, A. Bleier, Stability of aqueous $\alpha$-$Al_2O_3$ suspensions with poly (methacrylic acid) polyelectrolyte, J. Am. Ceram. Soc. 71 (1988) 250–255.

[33] J. Cesarano III, I.A. Aksay, Processing of concentrated aqueous $\alpha$-alumina suspensions stabilized with polyelectrolyte, J. Am. Ceram. Soc. 71 (1988) 1062–1067.

[34] G. Tari, J.M.F. Ferreira, O. Lyckfeldt, Influence of magnesia on colloidal processing of alumina, J. Eur. Ceram. Soc. 17 (1997) 1342–1350.

[35] G.W. Scherer, Theory of drying, J. Am. Ceram. Soc. 73 (1991) 3–14.