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Heterocoagulation moulding of alumina powder suspensions prepared using citrate dispersant

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Abstract

Coagulation characteristics of aqueous alumina suspensions prepared using di-ammonium hydrogen citrate (DHC) dispersant has been studied using MgO coagulating agent for direct coagulation casting (DCC). Mg–citrate complexes formed by the reaction between the DHC and MgO act as dispersant for alumina at pH near its iso-electric point. Setting of the alumina suspensions takes place, at MgO concentrations higher than the equivalent amount required to react with the DHC, by heterocoagulation of the alumina and MgO particles due to their opposite surface charges. The yield strength and Young's modulus of the wet-coagulated alumina bodies increased with aging time due to the hydration of the excess MgO. The minimum time required for mould removal decreases and yield strength and Young's modulus of the wet-coagulated bodies increases with MgO concentration. Alumina green bodies prepared at MgO concentrations in the range of 0.2–0.5 wt% sintered to ∼97% theoretical density at 1550 °C and the sintered ceramics showed more or less similar microstructures irrespective of MgO concentrations.

Keywords: C. Strength; D. Al_2O_3; D. MgO; Suspensions; Ammonium citrate; Direct coagulation casting

1. Introduction

Direct coagulation casting (DCC) is a relatively new near-net-ceramic shape forming process [1–3]. In conventional DCC processes, concentrated ceramic powder suspensions cast in a mould is converted in to strong coagulated bodies by destabilizing the suspensions by *in situ* generation of acid, base or electrolyte from soluble precursor molecules such as urea, acid anhydride, esters, lactones and hydroxyl aluminum diacetate [1–15]. Recently, the authors have reported a new coagulation method for alumina suspensions prepared using ammonium poly(acrylate) dispersant [16]. In this, MgO powder is used as a coagulating agent. Initially, the un-adsorbed ammonium poly(acrylate) dispersant present in the dispersion medium disperses the MgO coagulating agent along with the alumina powder. However, with time, the MgO reacts with the un-adsorbed ammonium poly(acrylate) and form Mg–poly(acrylate) nanoparticles. This resulted in desorption of the ammonium poly(acrylate) dispersant from alumina particle surface that leads to insufficient dispersant surface coverage and hence coagulation of the suspensions. The nanoparticles of Mg–poly(acrylate) distributed uniformly throughout the wet-coagulated body bind the alumina particles and provide strength and stability [16–18]. In addition, the MgO if used in excess of the amount required to react with the dispersant increase the yield strength and Young's modulus of the wet-coagulated bodies due to electrostatic attractive force between the alumina and MgO particles having opposite surface charges at the slurry pH [19]. The DCC process using MgO coagulating agent is established for yttria stabilized zirconia (YSZ) powder suspensions prepared using ammonium poly(acrylate) also [20].

When two colloidal suspensions containing particles with opposite surface charges on mixing, the charge on one type of particle counterbalance that on the other type with opposite sign, results in attraction between the particles. This is called heterocoagulation. In heterocoagulation, the particles with smaller size attracted towards the larger one results in coating of former on the later. There are few previous reports in which heterocoagulation of particle suspensions is effectively used in ceramic processing. Heterocoagulation is used for the coating of second phase on surface of particle/whiskers for ceramic composite processing [21–23]. Heterocoagulation coating of

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ceramic particles on polymer latex followed by consolidation and sintering results in porous ceramics with controlled pore size and pores size distribution [24]. Garcia-Perez et al. used heterocoagulation between submicron alumina and nanoparticle silica for fabrication of ceramic spheres of uniform size [24–27]. Heterocoagulation has also been used for either setting or to increase the strength of wet-coagulated bodies of YSZ or alumina powder suspensions prepared using ammonium poly(acrylate) dispersant [19,20].

It has been reported that viscosity and solids loading limit of alumina powder suspensions prepared using ammonium poly(acrylate) dispersant depend on the amount and molecular weight of the ammonium poly(acrylate) added [28]. Ammonium citrate is a well known dispersant used for preparation of aqueous ceramic powder suspensions [29–33]. The alumina suspensions prepared using an ammonium citrate dispersant shows lower viscosity at higher solids loading compared to that prepared using ammonium poly(acrylate) dispersant [34]. Suspensions with such higher solids loading is highly desirable for near-net-shape forming processes like direct coagulation casting. In the present work, coagulation characteristics of concentrated aqueous alumina suspensions prepared using ammonium citrate dispersant by MgO coagulating agent has been studied for direct coagulation casting. Mechanical properties of wet-coagulated bodies and micro structural features of sintered ceramics prepared at various MgO concentrations have been studied and results are presented. The mechanism of slurry setting is identified as heterocoagulation between alumina and MgO particles having opposite surface charges.

2. Experimental

A16SG alumina powder (Almatics, GmbH, Germany) of average particle size 0.40 μm and surface area 9.2 m^2/g was used. Di-ammonium hydrogen citrate (DHC) used as dispersant was procured from Aldrich Chemicals, USA. Analytical reagent grade light MgO powder (Thomas Baker, Mumbai) of surface area 32.1 m^2/g was used as coagulating agent. The MgO powder contains highly agglomerated flaky particles of size nearly 2–3 μm [17]. Distilled water was used for the preparation of slurries.

Slurries (50 vol%) were prepared by tumbling the alumina powder, water and various concentrations of the DHC dispersant in polyethylene bottles along with zirconia grinding media for 24 h. Viscosity of the slurries was measured using a Brookfield viscometer with a small sample adapter and cylindrical spindle (SC-21) to determine the optimum amount of dispersant required for dispersion of the powder. 55 vol% alumina slurries prepared at dispersant concentration of 0.3 wt% (based on alumina) was used for the study of coagulation characteristics and preparation of coagulated bodies. Various concentrations of MgO was added to the slurries and mixed well by ball milling. Viscosity of the slurries was measured at regular intervals after the addition of MgO. The viscosity measurement was taken using SC-28 spindle at a shear rate of 2.8 s^{-1}.

In order to understand the effect of cooling on coagulation, 55 vol% alumina slurries prepared in 200 ml polyethylene bottles were cooled to a temperature of ~5 °C in an ice bath. Various amounts of MgO powder was added to the ice cold alumina slurries and thoroughly mixed by ball milling at the ice cold condition for 20 min. In order to maintain low temperature (~5 °C) during milling, the slurries present in the smaller polythene containers were packed in bigger polyethylene containers with crushed ice and then subjected to milling on a roller mill. Immediately after mixing, viscosity of the slurries was measured at various times. The slurries were exposed to room temperature (~30 °C) during the viscosity measurements.

Variation of zeta potential and pH of alumina suspensions prepared in DHC dispersant solution with time after the addition of MgO was measured using a Zeta probe (Colloidal Dynamics, USA). 2 wt% alumina suspensions prepared in 0.005 mol/l DHC solution was used for the zeta potential measurements.

The 55 vol% alumina suspensions mixed with various concentrations of MgO at temperature of ~5 °C were degassed by applying vacuum and then cast in a closed cylindrical stainless steel moulds of 45 mm length and 22 mm diameter. The slurries cast in the moulds were removed at various time intervals to determine approximate time required for successful mould removal. The coagulated bodies removed from the mould were subjected to compressive stress–strain (Hounsfield, S-sires, UK) measurement in a universal testing machine at a cross-head speed of 2 mm/min. The compressive strength (yield stress) and Young's modulus of the wet-coagulated bodies were obtained from the Stress–strain graph [4,26,35].

The coagulated bodies prepared at various MgO concentrations were dried at 75% relative humidity at room temperature. The humidity condition was created in a desiccator using saturated sodium chloride solution. The coagulated bodies dried at room temperature to a constant weight were then heated in an air oven at 120 °C to remove the residual moisture. Shrinkage of the coagulated body during drying was calculated from its dimensions before and after drying. Density of the dried coagulated body was calculated from the weight and dimensions. The green bodies were sintered at 1550 °C for 2 h. The heating rate used was 5 °C/min. Density of the sintered alumina ceramics was determined by Archimedes method. Microstructure of sintered alumina ceramics prepared at various MgO concentrations was observed on fractured surfaces using a Scanning Electron Microscope (SEM, LEO 1455, UK).

3. Results and discussion

It has been reported that citrate dispersant adsorbs on alumina particle surface due to complex formation with the aluminum atoms on the particles surface [31]. Adsorption of citrate provides negative surface charge to the alumina particles. This results in a well dispersion of alumina powder in aqueous medium. A well dispersed alumina suspension is obtained at a minimum DHC concentration of 0.15 wt% at which the viscosity of the powder suspension decreased to a minimum value. It is well known that in DCC using MgO coagulating agent the reaction between the dispersant and MgO leads to coagulation and coagulation time depends on the concentration of dispersing agent. In order to have sufficient coagulation time, dispersant concentration higher than the optimum amount is normally used [16,17]. The alumina powder suspensions prepared using DHC dispersant showed only a marginal increase in viscosity by the addition of DHC beyond the optimum concentration up to 0.35 wt%. The 50 vol% alumina suspensions prepared at DHC concentration in the range of 0.15–0.35 wt% showed viscosity in the range of 0.15–0.285 Pa s, respectively at shear rate of 9.3 s^{-1}.

It has been noticed that the MgO dissolve in DHC solution up to DHC to MgO mol ratio 1:1 in 30 min at room temperature (30 °C). MgO powder added to the solution up to DHC to MgO mol ratio 1:1.5 leave a faint turbidity after 30 min that slowly disappears with time to form a clear solution at the end of 4 h. At DHC to MgO mol ratio above 1:1.5 the turbidity remains even after 24 h. The pH of the DHC solution was increasing from ~5.1 to 9.7 during dissolution of the MgO and a strong ammonia smell evolved from the solution. It is clear that the reaction between DHC dispersant and MgO produce soluble magnesium citrate complexes and ammonium hydroxide. It appears that the reaction takes place in two stages. In the first and fast stage, 1 mol of DHC reacts with 1 mol MgO to form a soluble complex. In the second stage, 2 mol of this complex further reacts slowly with 1 mol of MgO. The stoichiometric reactions are represented as below:

$$\begin{aligned}&2\mathrm{MgO} + 2\mathrm{HOOC{-}CH(OH)(CH_2{-}COONH_4)_2}\\&\xrightarrow{\text{Fast}} 2\mathrm{Mg[OOC{-}CH(OH)(CH_2{-}COO)](CH_2{-}COONH_4)}\\&+ 2\mathrm{H_2O} + 2\mathrm{NH_4OH}\end{aligned}$$

$$\begin{aligned}&2\mathrm{Mg[OOC{-}CH(OH)(CH_2{-}COO)](CH_2{-}COONH_4)}\\&\quad + \mathrm{MgO} \xrightarrow{\text{Slow}} \mathrm{Mg_3[OOC{-}CH(OH)(CH_2{-}COO)_2]_2}\\&\quad + 2\mathrm{NH_4OH}\end{aligned}$$

Fig. 1 shows effect of addition of various concentrations of MgO on viscosity variation with time of 55 vol% alumina suspensions prepared at 0.3 wt% DHC at room temperature (~30 °C). The viscosity measurements were taken at shear rate of 2.8 s^{-1} using SC-28 spindle. At 0.08 wt% MgO (DHC:MgO mol ratio 1:1.5, the amount of MgO required to react with whole –COO^- present in 0.3 g DHC), the viscosity of the suspension remains unchanged even after overnight aging. However, pH of the suspension increased from 9.2 to 10 in 1 h after the addition of MgO due to the ammonia formed by the reaction between DHC and MgO. At 0.106 wt% MgO (DHC:MgO mol ratio 1:2), viscosity of the suspensions increased from 1.5 to 4.5 Pa s in 7 h. Aging of this suspension overnight did not show further increase in viscosity. On the other hand, at MgO concentrations in the range of 0.2–0.5 wt%, suspension viscosity increased with time and reached a gel-like consistency (viscosity near 50 Pa s) in 3–0.75 h, respectively. It is clear that MgO concentration less than 0.2 wt% is not suitable for DCC of alumina suspension prepared at 0.3 wt% DHC dispersant.

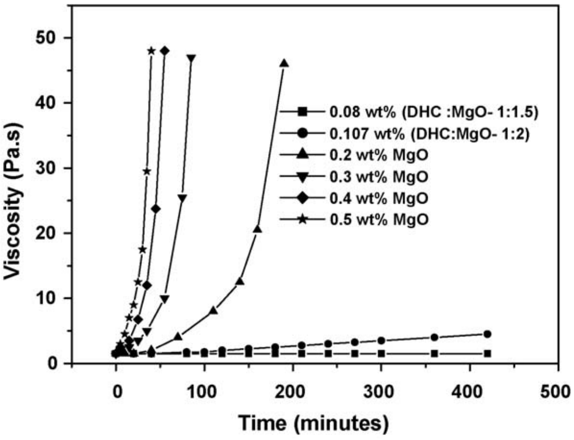

Fig. 1. Effect of addition of various concentration of MgO on viscosity variation with time of 55 vol% alumina suspensions prepared at 0.3 wt% DHC at room temperature (~30 °C).

When MgO powder is added to the alumina powder suspension prepared using DHC dispersant, the excess dispersant present in the suspension medium adsorb on the MgO particle surface and disperses them along with the alumina powder. It has been reported that alumina suspensions prepared using ammonium poly(acrylate) dispersant first showed increase in viscosity within few minutes after the addition of MgO due to heterocoagulation of alumina and MgO particle having opposite surface charges and then revert to the original viscosity value due to adsorption of the excess ammonium poly(acrylate) present in the dispersion medium on the MgO particles [16,17]. However, such a behavior is not observed in the case of alumina suspensions prepared using DHC dispersant. This implies that DHC molecules rapidly adsorb on MgO particles compared to ammonium poly(acrylate). Further, the MgO reacts with DHC to form soluble Mg–citrate complexes and ammonia. Fig. 2 shows variation of pH and zeta potential with time of alumina powder suspensions after the addition of various concentrations of MgO. The pH of the suspension increases rapidly with time in the initial few minute after the addition of MgO and thereafter slowly with time. At DHC to MgO mol ratios 1:1.5, 1:2 and 1:3 the suspension pH reached 9.2, 9.9 and 10.2, respectively in 1 h after the addition of MgO. On the other hand, at DHC:MgO mol ratio 1:1.5 the zeta potential value decreased slowly from −68 to −61 mV in 1 h. However, at higher MgO concentrations, the decrease in zeta potential is rapid in the first 10 min and then slows. At DHC to MgO mol ratios 1:2 and 1:3 the zeta potential values decreased to −43 and −31 mV, respectively in 1 h after addition of MgO. At DHC to MgO mol ratio 1:1.5, whole MgO is consumed due to reaction with DHC. The slight decrease in zeta potential observed did not affect the suspension stability. It is well known that at pH nearly 10, alumina particles have negative and MgO particles have positive surface charges, respectively [37,39]. Therefore, large decrease in zeta potential values at higher MgO concentrations is due to heterocoagulation of alumina and unreacted MgO particles having opposite surface charges. It is clear that the Mg–citrate complexes formed by the reaction between DHC dispersant and MgO did

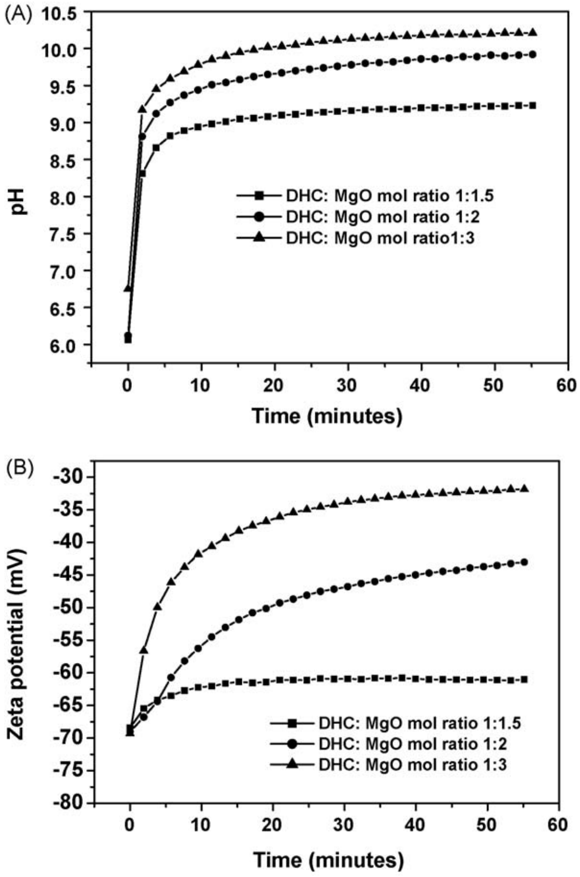

Fig. 2. Variation of pH (A) and zeta potential (B) with time of alumina powder suspensions after the addition of various concentrations of MgO.

not change the surface characteristics of MgO particles though it acts as dispersant for alumina particles at pH nearly 10. The heterocoagulation of alumina and MgO particles leads to setting of the powder suspensions.

It is well known that iso-electric point of alumina is ~9 and the alumina powder did not disperse by electrostatic mechanism at pH near its iso-electric point (pH 8–11) [36,37]. It is expected that 0.08 wt% MgO (equivalent to react with the dispersant) desorbs whole amount of DHC dispersant from alumina particle surface and coagulate the alumina suspension. Contrary to this, at 0.08 wt% MgO, the suspension viscosity remains unchanged even after overnight aging. This indicates that the Mg–citrate complex formed by the reaction between DHC and MgO acts as dispersant for alumina. Effect of magnesium citrate on aqueous dispersion of alumina powder has been already reported by Yang and Sigmund [34]. This is further confirmed by the fact that the alumina powder disperses well in Mg–citrate complex solution prepared by dissolving 1.5 mol MgO powder in 1.0 mol DHC solution. Fig. 3 shows viscosity versus shear rate plot of 55 vol% alumina suspension prepared in DHC solution and Mg–citrate complex solution. The suspension prepared in Mg–citrate complex solution showed slightly low viscosity compared to that prepared in DHC solution. This is in agreement with the observation made by Yang et al. that highly loaded aqueous alumina suspensions with low viscosity at ambient temperature (25 °C) is formed in presence of ammonium citrate–magnesium citrate combination [34]. However, the mechanism by which the magnesium citrate enhances alumina powder dispersion is not disclosed. It appears that more than one citrate ions associate through complex formation with Mg^{2+}ions results in molecular size sufficient to provide semisteric stabilization. Low viscosity of alumina suspensions in presence of magnesium citrate is attributed to the combination of electrostatic and semisteric contributions towards particle stabilization.

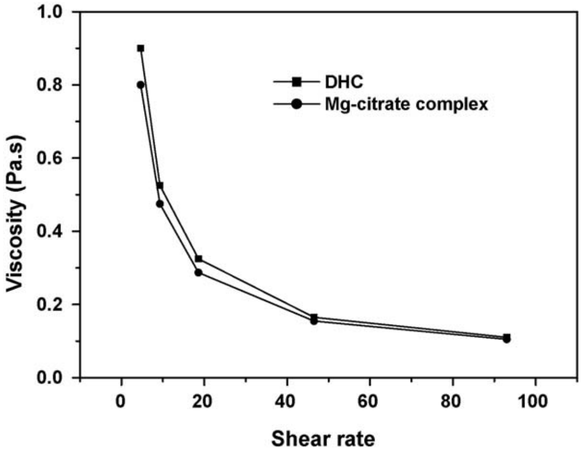

Fig. 3. Viscosity versus shear rate plot of 55 vol% alumina suspension prepared in DHC solution and Mg–citrate complex solution.

In DCC process, the slurry viscosity should remain more or less constant for sufficient period of time after addition of coagulating agent for proper mixing and degassing before casting. However, in the present case, at room temperature, the slurry viscosity showed continuous increase after the addition of MgO, except at 0.2 wt% MgO. At 0.2 wt% MgO, the slurry viscosity remains more or less constant up to 40 min. It is well known that cooling of slurry to temperature of ~5 °C before addition of MgO and maintaining the same temperature during mixing keeps the slurry viscosity more or less constant for sufficient time. Fig. 4 shows viscosity variation with time of 55 vol% alumina slurry mixed with various concentrations of

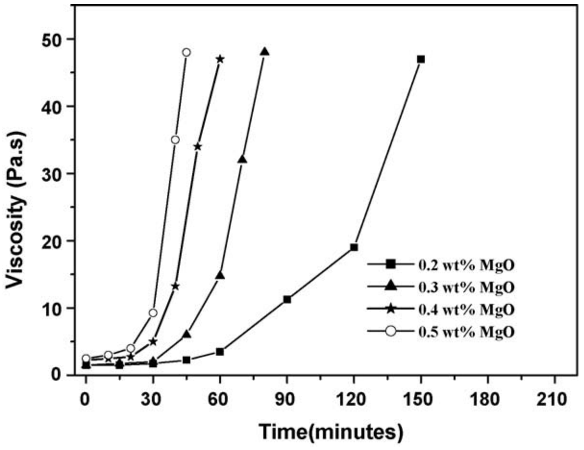

Fig. 4. Viscosity variation with time of 55 vol% alumina slurry mixed with various concentrations of MgO (mixing at ~5 °C).

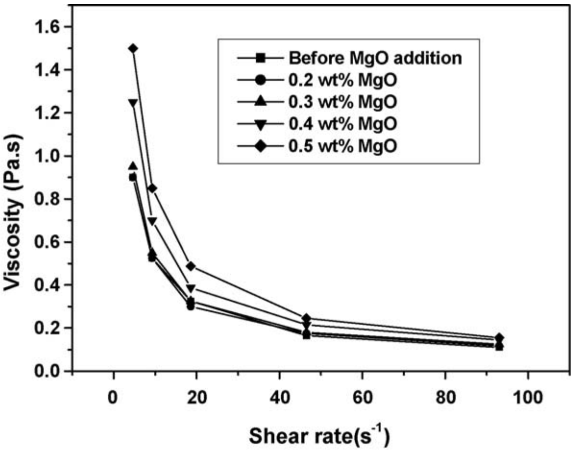

Fig. 5. Viscosity versus shear rate plot of DCC slips prepared at various MgO concentrations.

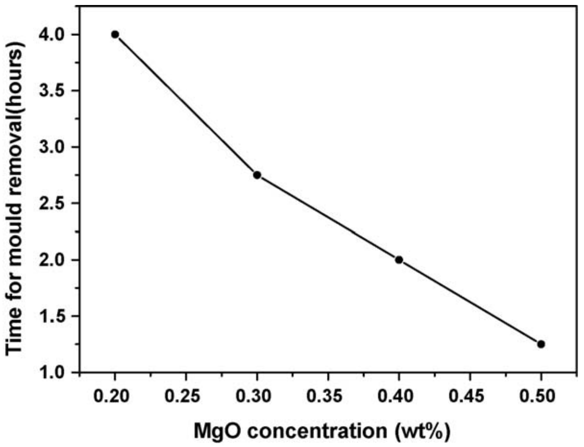

Fig. 6. Mould removal time versus MgO concentration.

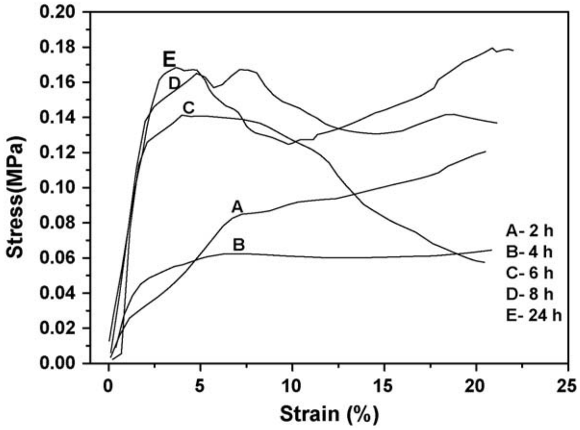

Fig. 7. Stress–strain behavior of the wet-coagulated bodies removed from the mould after various aging time (MgO concentration 0.4 wt%).

MgO at ~5 °C. The measurements were taken at shear rate of 2.8 s^{-1} using SC-28 spindle and the slurries were exposed to room temperature throughout the measurement process. Viscosity of slurries containing 0.2–0.5 wt% MgO remains more or less constant for time period in the range of 30–15 min after mixing with MgO. This much time is sufficient to carryout degassing and casting of the slurries. It has been observed that the viscosity of slurries kept in ice bath after mixing with MgO remains more or less constant for more than 1 h. Therefore, more working time, if required, could be obtained by maintaining the slurry temperature ~5 °C by keeping them in ice bath during degassing process.

Fig. 5 shows viscosity versus shear rate plot of DCC slips prepared at various MgO concentrations. Viscosity measurements were taken immediately after mixing the slurries with MgO at ~5 °C for 20 min. The slurries showed pseudoplastic flow behavior. The slurries containing 0.2 and 0.3 wt% MgO showed more or less same viscosity as that of slurry before addition of MgO. Further increase in MgO concentration increased both viscosity and pseudoplastic behavior of the slurries. However, viscosity of the DCC slips prepared at the four MgO concentrations are within the limit (less than 1 Pa s at shear rate 9.3 s^{-1}) suitable for casting in any intricate shape mould. The yield stress value (calculated using the Casson model) of the 55 vol% alumina slurry marginally increased from 2.8 to 3 Pa up on the addition of MgO up to 0.3 wt% [38]. However, the DCC slips containing MgO concentrations of 0.4 and 0.5 wt% showed relatively higher yield stress values of 4.06 and 5.46 Pa, respectively. The slurries with this low yield stress values could flow in to any intricate shape of a mould.

Though the slurries containing 0.2–0.5 wt% MgO cast in moulds attain gel-like consistency (viscosity ~50 Pa s) at time in the range of 2.5–0.75 h (Fig. 4), removal of gelled bodies without deformation require higher aging time. The approximate time required for mould removal without deformation is shown in Fig. 6. The slurries prepared at MgO concentration in the range of 0.2–0.5 wt% require approximately 4–1.25 h for mould removal after casting. Fig. 7 shows stress–strain behavior of the wet-coagulated bodies prepared from DCC slip at 0.4 wt% MgO and removed from the mould after various aging time. The wet-coagulated bodies in general showed elastic deformation up to the yield point. The wet-coagulated body removed after 2 h showed plastic deformation with considerable strain hardening effect after the yield point. The wet-coagulated body removed at 4 h showed more or less constant stress value after the yield point indicating that the stress is relived by formation of cracks. The wet-coagulated bodies removed from the mould after aging for more than 6 h showed typical brittle failure after the yield pint. The yield strength and Young's modulus of the wet-coagulated bodies increased from 34 to 168 kPa and 2.5 to 39 MPa, respectively when the aging time increased from 2 to 8 h. Thereafter, increase in yield strength is marginal. However, the Young's modulus showed a considerable increase to 74 MPa at aging time of 24 h. Fig. 8 shows yield strength and Young's modulus of wet-coagulated bodies at 0.4 wt% MgO and removed from mould after various aging time.

Fig. 9 shows stress–strain plot of wet-coagulated bodies prepared at various MgO concentrations removed from the mould after 24 h aging. The wet-coagulated body prepared at MgO concentration in the range of 0.2–0.5 wt% showed elastic deformation up to the yield point. After the yield point, the

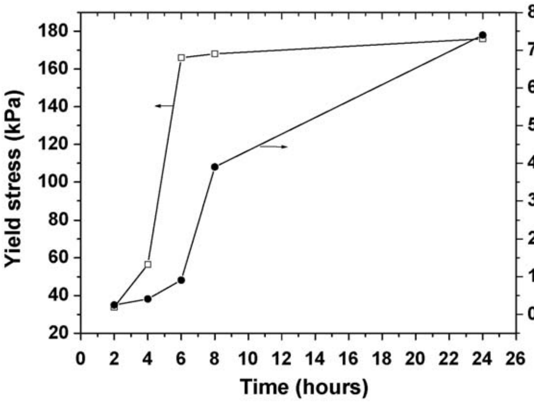

Fig. 8. Yield strength and Young's modulus of wet-coagulated bodies removed from mould after various aging time (MgO concentration 0.4 wt%).

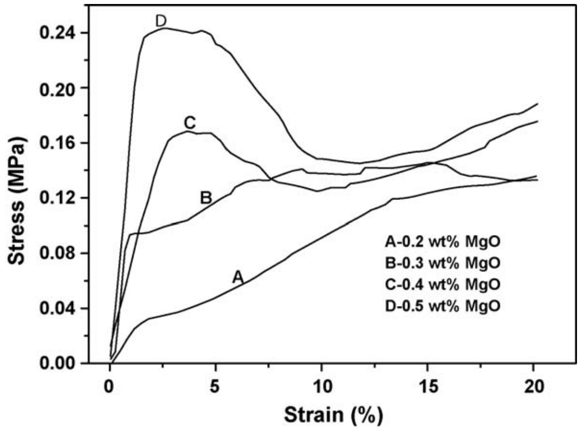

Fig. 9. Stress–strain plot of wet-coagulated bodies prepared at various MgO concentrations removed from the mould after 24 h aging.

wet-coagulated bodies prepared at 0.2 and 0.3 wt% MgO showed plastic deformation with strain hardening. However, wet-coagulated bodies prepared at MgO concentrations of 0.4 and 0.5 wt% showed typical brittle failure. Brittle nature of the wet-coagulated bodies increased with increase in concentration of MgO. Fig. 10 shows photograph of wet-coagulated bodies after the stress–strain measurement. Increase in brittle nature of the wet-coagulated bodies with increase in MgO concentration is clear in the photograph. The yield strength and Young's modulus of wet-coagulated bodies prepared at various MgO concentration is shown in Fig. 11. The yield strength and Young's modulus increased from 30 to 230 kPa and 2.5 to 103 MPa, respectively when the MgO concentration increased from 0.2 to 0.5 wt%. Relatively high yield strength and Young's modulus facilitate easy removal of wet-coagulated bodies from the mould without any deformation. Increase in strength and Young's modulus of the wet-coagulated bodies with increase in MgO concentration is due to increase in electrostatic attractive force offered by larger number of MgO particles. In addition, the heterocoagulation results in less homogeneous particle network in the wet-coagulated bodies that leads to higher strength and Young's modulus [19,40]. Increase in MgO concentration decrease the homogeneity of particle network in the wet-coagulated bodies. This also contributes to increase in strength and modulus with increase in MgO concentration.

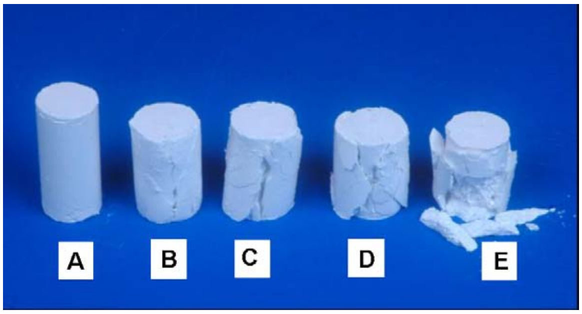

Fig. 10. Photograph of wet-coagulated bodies before (A) and after (B–E) the stress–strain measurement. B: 0.2 wt% MgO; C: 0.3 wt% MgO; D: 0.4 wt% MgO; E: 0.5 wt% MgO.

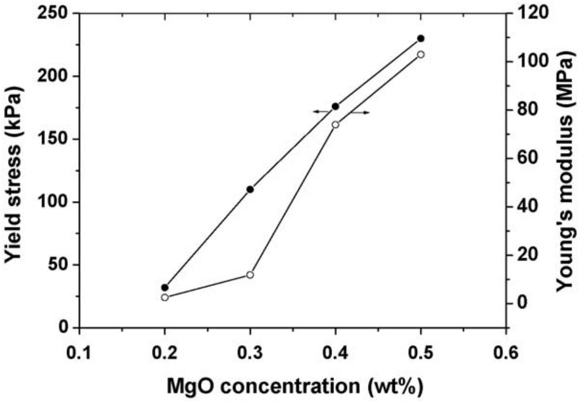

Fig. 11. Yield strength and Young's modulus of wet-coagulated bodies prepared at various MgO concentration.

It has been reported that polycrystalline MgO undergoes hydration when aged in water [41]. The hydration process starts at the grain boundaries. Due to the volume expansion during the hydration process, the polycrystalline MgO disintegrate in to smaller grains and finally to monocrystals [41]. Conversion of polycrystalline MgO in to monocrystals results in increase in surface area and that eventually leads to increase in number of positive surface charges. In addition, the hydration process results in increase in volume of MgO. Increase in strength and Young's modulus of wet-coagulated bodies with time is due to hydration of unreacted MgO present in the wet-coagulated body.

As the DHC dispersant rapidly adsorb on the MgO coagulating agent compared to the ammonium poly(acrylate) dispersant, the MgO coagulating agent easily mixes with the DHC dispersed alumina slurry compared to the ammonium poly(acrylate) dispersed alumina slurry. The DCC alumina suspensions prepared using DHC dispersant showed lower viscosity and yield stress values compared to that prepared using ammonium poly(acrylate) dispersants. Therefore, DCC alumina suspensions of higher solids loading is possible with DHC dispersant (55 vol%) than with ammonium poly(acrylate) dispersant (~53 vol%). On the other hand, at same MgO concentrations, the wet-coagulated bodies obtained from 53 vol% alumina slurries prepared using ammonium poly(acrylate) dispersant showed higher yield strength and Young's modulus compared to that obtained from 55 vol% alumina slurries prepared using DHC dispersant. Electrostatic attraction between the alumina particles and unreacted MgO having opposite surface charges is common in both DHC and ammonium poly(acrylate) system. Therefore, higher yield strength and Young's modulus of wet-coagulated bodies obtained from alumina suspensions prepared using ammonium poly(acrylate) dispersant is due to the magnesium poly(acrylate) nanoparticles, formed by the reaction between ammonium poly(acrylate) and MgO, that binds the alumina particles [16–19].

The gelled bodies did not show any deformation or crack during drying at room temperature at 75% relative humidity. The cylindrical bodies prepared from DCC slip at MgO concentrations in the range of 0.2–0.5 wt% showed very close values of drying shrinkage, green density, and sintering shrinkage, but did not follow any regular trend. The drying shrinkage, green density and sintering shrinkage values observed are in the ranges of 2.9–2.6%, 56.3–57.2% TD (theoretical density), and 15.4–16.1%, respectively. It has been reported that increasing MgO content in alumina beyond 0.25 wt% resists sintering of pores due to formation of spinel phase [42]. However, the green bodies prepared by the DCC process at MgO concentration in the range of 0.2–0.5 wt% achieve a density of ~97% TD at 1550 °C. Further, the sintered alumina ceramics prepared at MgO concentration in the range of 0.2–0.5 wt% showed more or less similar microstructures. Fig. 12 shows SEM photomicrographs of sintered alumina ceramics prepared by DCC at various MgO concentrations.

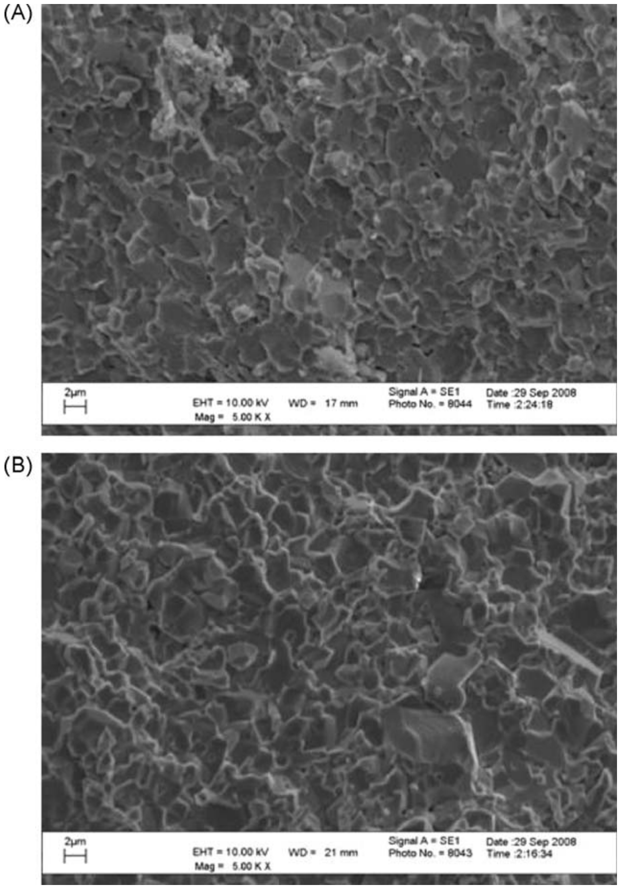

Fig. 12. SEM microstructure of fractured surface of sintered alumina ceramics prepared by the DCC at (A) 0.2 wt% MgO and (B) 0.5 wt% MgO.

4. Conclusions

Direct coagulation casting of aqueous alumina suspensions prepared using di-ammonium hydrogen citrate (DHC) dispersant by a MgO coagulating agent has been studied. The Mg–citrate complex formed by the reaction between MgO and DHC acts as dispersant for alumina at pH near its iso-electric point. Setting of the alumina suspensions takes place at MgO concentrations higher than the equivalent amount required to react with the DHC dispersants by heterocoagulation of alumina and excess MgO particles present in the suspension medium due to their opposite surface charges at the suspension pH. The yield strength and Young's modulus of the wet-coagulated body increased with aging time due to hydration of the excess MgO. The minimum time required for mould removal decreased from 4 to 1.25 h when MgO concentration increased from 0.2 to 0.5 wt%. Yield strength and Young's modulus of wet-coagulated alumina bodies increased from 30 to 230 kPa and 2.5 to 103 MPa, respectively when the MgO concentration increased from 0.2 to 0.5 wt%. The sintered alumina ceramics prepared at MgO concentrations in the range of 0.2–0.5 wt% showed ~97% TD and more or less similar microstructures irrespective of MgO concentrations.

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References

[1] 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.

[2] 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.

[3] J.A. Gauckler, T.J. Graule, F. Baader, Ceramic forming using enzyme catalyzed reactions, Mater. Chem. Phys. 61 (1999) 78–102.

[4] D. Hesselbarth, E. Tervoort, C. Urban, L.J. Gauckler, Mechanical properties of coagulated wet particle net-works with alkali swellable thickeners, J. Am. Ceram. Soc. 84 (2001) 1689–1695.

[5] 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.

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

[7] 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.

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

[9] 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.

[10] A.L. Penard, F. Rossignol, H.S. Nagaraja, C. Pagnoux, T. Chartier, Dispersion of α-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.

[11] 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.

[12] 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.

[13] 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.

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

[15] J.G.P. Binner, A.M. McDermott, 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.

[16] 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.

[17] K. Prabhakaran, C.S. Kumbhar, R. Sooraj, N.M. Gokhale, S.C. Sharma, Effect of concentration of ammonium poly(acrylate) dispersant and MgO on coagulation characteristics of aqueous alumina direct coagulation casting slurries, J. Am. Ceram. Soc. 91 (2008) 1993–1998.

[18] K. Prabhakaran, R. Sooraj, A. Melkeri, N.M. Gokhale, S.C. Sharma, A new direct coagulation casting process for alumina slurries prepared using poly(acrylate) dispersant, Ceram. Int. 35 (2009) 979–985.

[19] K. Prabhakaran, S.P. Tambe, A. Melkeri, N.M. Gokhale, S.C. Sharma, Mechanical properties of wet-coagulated alumina bodies prepared by direct coagulation casting using MgO coagulating agent, J. Am. Ceram. Soc. 91 (2008) 3608–3612.

[20] K. Prabhakaran, A. Melkeri, N.M. Gokhale, T.K. Chongdar, S.C. Sharma, Direct coagulation casting of YSZ powder suspensions using MgO as coagulating agent, Ceram. Int. 35 (2009) 1487–1492.

[21] T. Garino, Heterocoagulation as an inclusion coating technique for ceramic composite processing, J. Am. Ceram. Soc. 75 (1992) 514–518.

[22] S.J. Wu, L.C. Dejonghe, Alumina-coated hollow glass spheres/alumina composites, J. Mater. Sci. 32 (1997) 6075–6084.

[23] N. Garmendia, I. Santacruz, R. Moreno, I. Obieta, Slip casting of nanozirconia/MWCNT composites using heterocoagulation process, J. Eur. Ceram. Soc. 29 (2009) 1939–1945.

[24] F. Tang, H. Fudouzi, T. Uchikoshi, Y. Sakka, Preparation of porous materials with controlled pore size and porosity, J. Eur. Ceram. Soc. 24 (2004) 341–344.

[25] P. Garcia–Perez, C. Pagnoux, F. Rossignol, J.F. Baumard, Heterocoagulation between SiO_2 nanoparticles and Al_2O_3 submicronparticles; influence of the background electrolyte, Colloids Surf. A 281 (2006) 58–66.

[26] P. Garcia-Perez, C. Pagnoux, A. Pringuet, A. Videcoq, J.F. Baumard, Agglomeration of alumina submicron particles by silica nanoparticles: application to processing spheres by colloidal route, J. Colloid Interface Sci. 313 (2007) 527–536.

[27] C. Pagnoux, N. Tessier-Doyen, A. Pringuet, M. Cerbelaud, P. Garcia-Perez, Influence of the suspension flocculated state on the microstructure of alumina spheres elaborated by colloidal granulation, J. Eur. Ceram. Soc. 29 (2009) 1379–1385.

[28] H. Okamoto, M. Hashiba, Y. Nurishi, K. Hiramatsu, Fluidity and dispersion of alumina suspensions at the limit of thickening by ammonium poly(acrylate), J. Mater. Sci. 26 (1991) 383–387.

[29] I. Santacruz, K. Anapoorni, J. Binner, Preparation of high solids content nano zirconia suspensions, J. Am. Ceram. Soc. 91 (2008) 398–405.

[30] E. Ewais, A.A. Zaman, W. Sigmund, Temperature induced forming of zirconia from aqueous slurries: mechanism and rheology, J. Eur. Ceram. Soc. 22 (2002) 2805–2812.

[31] P.C. Hidber, T.J. Graule, L.J. Gauckler, Citric acid—a dispersant for aqueous alumina suspensions, J. Am. Ceram. Soc. 79 (1996) 1857–1867.

[32] E.P. Luther, J.A. Yanez, G.V. Franks, F.F. Lange, Effect of ammonium citrate on the rheology and particle packing of the alumina slurries, J. Am. Ceram. Soc. 78 (1995) 1495–1500.

[33] S. Dhara, P. Bhargava, Influence of nature and amount of dispersant on rheology of aged aqueous alumina gelcasting slurries, J. Am. Ceram. Soc. 88 (2005) 547–552.

[34] Y. Yang, W.M. Sigmund, A new approach to prepare highly loaded aqueous alumina suspensions with temperature sensitive rheological properties, J. Eur. Ceram. Soc. 23 (2003) 252–261.

[35] B. Balzer, 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.

[36] J.S. Reed, Principles of Ceramic Processing, second ed., John Wiley and Sons, Inc., New York, 1995.

[37] M.D. Robinson, J.A. Pask, W. Fuerstenau, Surface charge of alumina and magnesia in aqueous medium, J. Am. Ceram. Soc. 47 (1964) 516–520.

[38] 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.

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

[40] H.M. Wyss, E. Elena, V. Tervoort, L.J. Gauckler, Mechanics and microstructure of concentrated particle gels, J. Am. Ceram. Soc. 88 (2005) 2337–2348.

[41] R. Salomao, L.R.M. Bittencourt, V.C. Pandolfelli, A novel approach for magnesia hydration assessment in refractory castables, Ceram. Int. 33 (2007) 803–810.

[42] S.R. Shah, A.H. Chokshi, R. Raj, Porous Al_2O_3-spinel based poly crystals that resists free sintering, J. Am. Ceram. Soc. 91 (2008) 3451–3454.