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Preparation of extrudable alumina paste by coagulation of electrosterically stabilized aqueous slurries

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Abstract

The present work demonstrates the conversion of a low viscous concentrated (55 vol.%) alumina slurry into a thick extrudable paste by in situ coagulation. Highly concentrated (55 vol.%) electrosterically stabilized aqueous alumina slurry prepared using polyacrylate dispersant was coagulated by in situ generation of acetic acid. Acetic anhydride was used for acid generation and the miscibility of acetic anhydride in aqueous medium was increased by polyethylene glycol. Addition of acetic anhydride >0.16 mol/l converts the slurry in to a stiff paste, within 5 min. The paste exhibits extrudable consistency. Incorporation of 1% PVA in the slurry provides additional strength to the extruded tubes against deformation and development of drying cracks. The tubes sintered to 97% TD and the sintered samples showed a fine grained microstructure. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Coagulation; Extrusion; Suspensions

1. Introduction

Ceramic paste that is having high solids loading is extremely important for extrusion, injection molding, and rolling and jiggering processes.[1–5] They are usually prepared by mechanically mixing the ceramic powder with water and suitable polymer binder.[6,7] Such technique requires heavy machinery, as an example, high intensity mixture, in which the problem of contamination arises. Inhomogeneous distribution of binder, moisture and the elimination of hard agglomerates are also likely.[8,9] Colloidal processing is a proven method, which provides highly loaded and un-agglomerated ceramic powder suspensions in aqueous medium. The conversion of this powder suspension into a paste, by controlling the surface forces, offers an alternative, energy efficient process. Concentrated powder suspensions are prepared by either adjusting the pH away from isoelectric point or by adding polyelctrolytes.[10–12] In the former case, the particles are stabilized in aqueous medium by electrostatic repulsion and in the later case by both electrostatic and sterric mechanisms. Consolidation of electrostatically stabilized alumina suspensions into saturated cakes is generally achieved by pressure filtration, which results in brittle bodies. Chang et al. demonstrated that the addition of excess electrolyte to these suspension results in short range repulsion between particles and the saturated bodies, obtained by pressure filtration, shows plastic behaviour.[13–15] However, addition of salt in a concentrated suspension results in localized gelation and introduces high degree of inhomogeneity. In actual practice, excess electrolyte is added to the dilute suspensions and then consolidation into a saturated body by pressure filtration is followed. These consolidated bodies are further processed to a near-net-shape component by vibro-forming or as layered composite structure by rolling.[16] Graule et al. demonstrated the conversion of highly loaded electrostatically stabilized ceramic powder suspensions into near-net-shape plastic gels by urase catalysed in situ hydrolysis of urea.[17,18] Although, electrosterically stabilized powder suspensions prepared using polyelectrolytes produce high solid loading, their consolidation by coagulation is less attempted. The present work reports on the coagulation behaviour of highly concentrated, electrosterically stabilized alumina suspension by in situ generation of acid and the extrusion characteristics of the resulting paste.

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2. Experimental

A16SG alumina powder (ACC — Alcoa, Calcutta) of average particle size 0.34 μm and surface area 10.4 m^2/g was used as the starting material. Other chemicals used were acetic anhydride (s.d. Fine Chemicals, India) and polyethylene glycol (s.d. Fine Chemicals, India, molecular weight — 300). Acetic anhydride was purified by distillation before use. Doubly distilled water was used for the preparation of dispersions. Darvan 811(R.T Vaderbilt company Inc., average molecular weight — 5000), a 43% solution of sodium polyacrylate was used as dispersant. Polyvinyl alcohol (Aldrich chemical) with an average molecular weight 13,000–23,000 was used as the binder. Reagent grade ammonia solution and acetic acid were used for pH adjustments. The slurry was prepared by milling alumina powder in aqueous medium with the dispersant in a polyethylene container for 4 h using zirconia grinding media. A dispersant concentration of 0.3 mg/m^2 of alumina surface was added. The slurry viscosity was measured using Brookfield viscometer at shear rates ranging from 4.65 to 93 s^{-1}. A 25 wt.% solution of acetic anhydride in polyethylene glycol was separately prepared. Various amounts of the acetic anhydride solution was added to the alumina slurries kept in an ice bath under constant stirring. The time when the slurry has lost its flow property was noted as coagulation time. The rheological characteristics of pastes obtained by coagulation was studied by using Torque rheometer (Brabander plasticorder, Model PLE 651) at shear rates ranging from 9.5 to 38 s^{-1}. The paste was extruded into tubes in a laboratory model vertically mounted plunger type extruder. The tubes were dried at 65% relative humidity at 45°C. The density of the green bodies were measured by mercury displacement method. The green tubes were sintered at 1500°C for 2 h. The typical sintering schedule involves, heating from ambient temperature to 300°C at 3°C/min, from 300 to 900°C at 5°C/min and from 900 to 1500°C at 10°C/min. The density of the sintered specimens were measured by Archemides' principle. The microstructure of sintered samples were examined on a fractured surface with a scanning electron microscope (Hitachi 2042, Japan).

3. Results and discussion

The stability of alumina slurries dispersed in aqueous medium using polyacrylate dispersants is governed by both electrostatic repulsion between the negative charges developed by the ionization of –COONa groups on the adsorbed polymer molecules and the steric repulsion between the adsorbed polymer chains.[12] Fig. 1 shows the viscosity of 55 vol.% aqueous alumina slurry, prepared by using the polyacrylate dispersant, at various shear rates. The slurry shows 'shear thinning' flow behaviour with viscosity values in the range 2–0.24 Pa s at shear rates in the range 4.65–93 s^{-1}. Since the 55 vol.% slurry exhibits very high viscosity at pH below 8, the slurry consisting of 40 vol.% alumina was used for studying the influence of pH on viscosity behaviour. Fig. 2 shows the change in viscosity of 40 vol.% of alumina slurry with respect to pH. The viscosity of the slurry is low when the pH is above 9 but increases gradually with decrease of pH up to 8.4. The slurry at pH below 8.4 showed a rapid increase in viscosity with loss

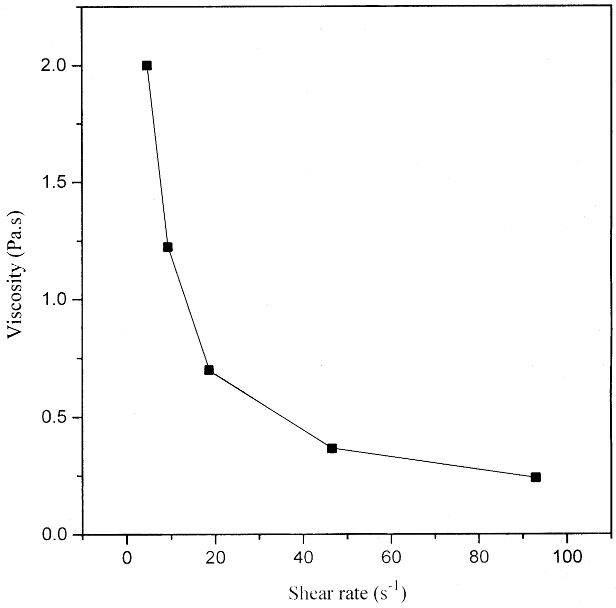

Fig. 1. Viscosity of 55 vol.% alumina slurry prepared by using the polyacrylate dispersant (pH 9.5) at various shear rates.

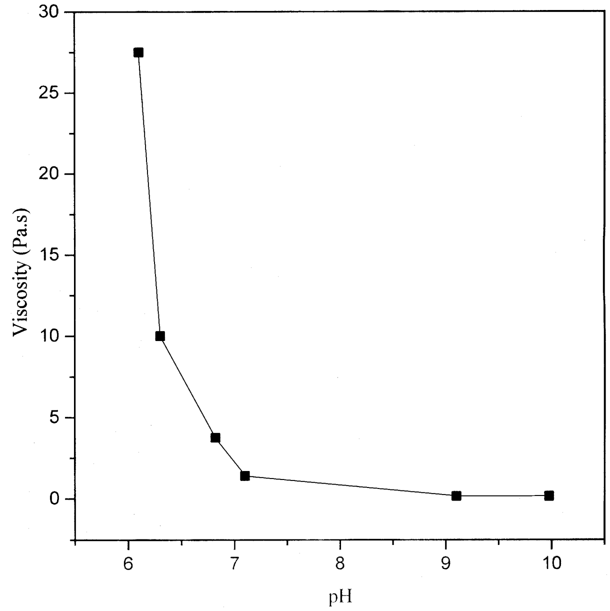

Fig. 2. Effect of pH on the viscosity of aqueous alumina slurry prepared by using the polyacrylate dispersant (solids loading 40 vol.%).

of the flow property at pH below 7. When the slurry pH decreases, the completely ionisable –COONa groups on the adsorbed polymer chain are converted in to weakly ionisable –COOH groups, which minimize the electrostatic repulsion between the alumina particles. Moreover, in acidic medium, the steric repulsion is replaced with attractive force between particles by bridging of adsorbed polymer chains through inter chain hydrogen bonding between –COOH groups. This converts the powder suspension into a 'gel' and the gelation mechanism is schematically represented in Fig. 3. The addition of acid into a highly concentrated suspension (55 vol.%) resulted in localized gelation, which involved the risk of inhomogeneous mixing. Therefore, the in situ generation of acid was attempted with acetic anhydride, selected as an acid source. It was noted that acetic anhydride is only partially miscible in aqueous medium. However, a mixture of acetic anhydride and polyethylene glycol was found to be completely miscible with water. In addition to that, the polyethylene glycol acts as a lubricant for the extrusion process.[19] Hence, a mixture of acetic anhydride and polyethylene glycol was used for the subsequent studies.

Acetic anhydride undergoes hydrolysis in aqueous medium and produces acetic acid.

$$(CH_3-CO)_2O + H_2O \rightarrow 2CH_3-COOH$$

Hydrolysis of acetic anhydride in aqueous alumina slurry not only decreases the pH but also increases the electrolyte concentration and thereby minimizes the repulsive force between particles. This coagulates the alumina slurry to a stiff mass. Fig. 4 shows the variation of gelation time of 55 vol.% alumina slurry with acetic anhydride concentration (expressed with respect to the dispersion medium). At ambient temperature (~30°C) the hydrolysis of acetic anhydride is highly rapid, so that the gelation of alumina slurry takes place immediately. The time of gelation is controlled by the critical concentration of acetic anhydride and the gelation time is extended up to 10 min at a concentration of 0.12 mol/l. However, the coagulated mass obtained at this concentration showed shear induced flow and it is necessary to strengthen the coagulated mass for obtaining extrudable alumina paste. This could be achieved by increasing the acetic anhydride concentration. A stiff and plastic coagulated mass was obtained at minimum acetic anhydride concentration of 0.16 mol/l in which the gelation time was only 2 min. Preparing the paste at low temperatures preferably in an ice bath may also extend the gelation time. The slurry containing 0.16–0.25 mol/l acetic anhydride shows a gelation time of 5–3 min at 5°C. The variation of pH of the slurry having acetic anhydride concentration of 0.16 mol/l with time at 30 and 5°C is shown in Fig. 5. At 30°C, the slurry pH decreases from 10.3 to 6.6 within 2 min and becomes a stiff mass due to coagulation. On the other hand, at 5°C, the slurry pH decreases from 8.8 to 7.3 in 5 min and only after 5 min the slurry coagulated to a stiff mass: The lower rate of pH decrease observed at 5°C was due to the lower rate of hydrolysis of acetic anhydride.

The acetic anhydride concentration of 0.25 mol/l was selected for the preparation of alumina paste for extrusion studies. At this concentration of acetic anhydride, the concentration of polyethylene glycol was approximately 2.5 wt.% of alumina. Similarly, an equivalent

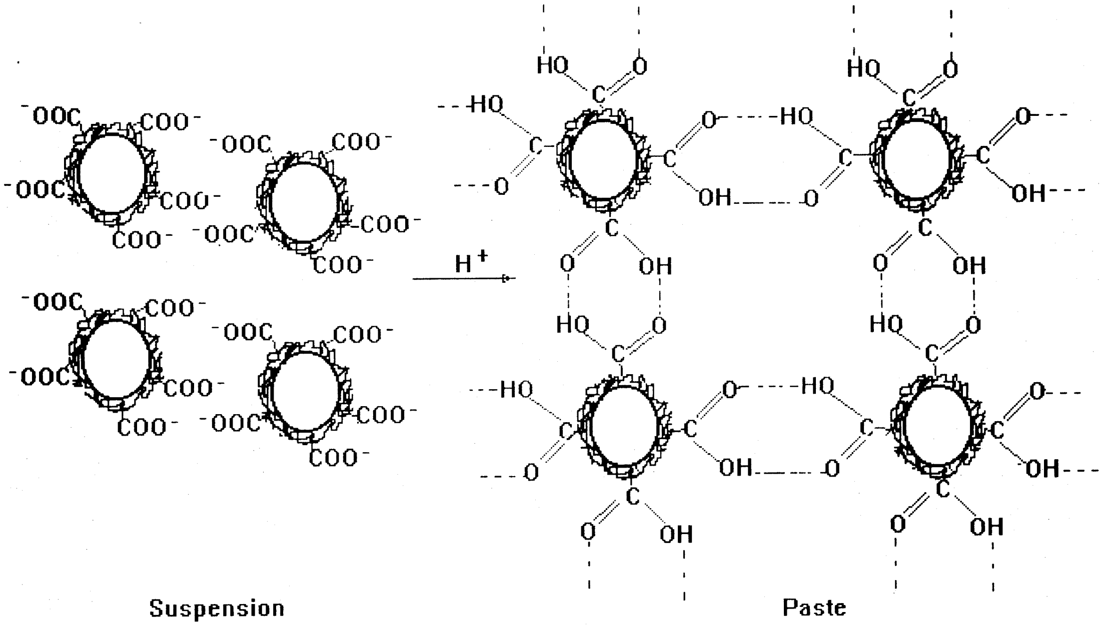

Fig. 3. Schematic representation of the mechanism of gelation in aqueous alumina slurry prepared by using polyacrylate dispersant.

amount of acetic acid was directly added to form a paste for comparison. Fig. 6 shows the viscosity of both these alumina pastes having 55 vol.% of solids at various shear rates. The viscosity of both the pastes fall with increasing shear rate which is characterised as 'shear thinning' flow behaviour. However, the paste prepared by in situ generation of acid shows lower viscosity compared to that of the pastes prepared by direct addition of acetic acid. The viscosity value of alumina paste obtained by in situ generation of acid is in the range 12–3.3 k Pa s at shear rate in the range 9.5–38 s^{-1}. The in situ generation of acid induces more homogeneous gelation of the alumina slurry which results in the low viscosity. Shear stress- shear rate plot for both the alumina pastes is shown in Fig. 7. The paste prepared by in situ generation of acid shows lower shear stress compared to that of the paste prepared by direct addition of acid. Also, the increase in shear stress with shear rate is higher for alumina paste prepared by the external addition

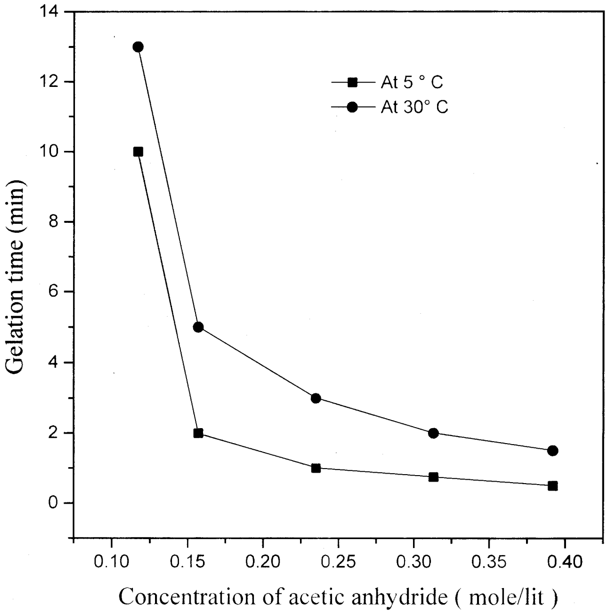

Fig. 4. Effect of acetic anhydride concentration and the temperature on gelation time of aqueous (55 vol.%) alumina slurry prepared by using the polyacrylate dispersant.

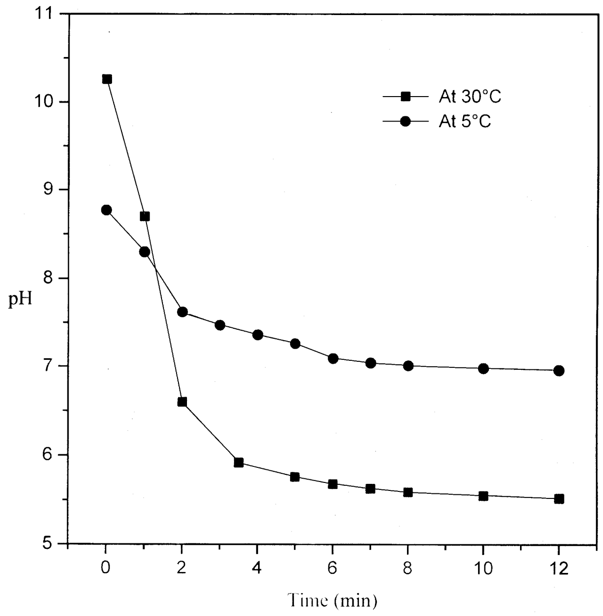

Fig. 5. Variation of pH with time of a 55 vol.% alumina slurry, prepared by using the polyacrylate dispersant, upon the addition of acetic anhydride (acetic anhydride concentration 0.16 mol/l).

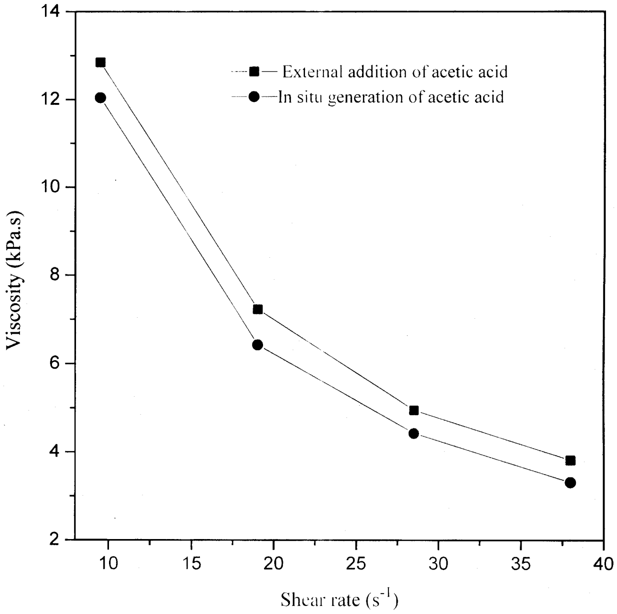

Fig. 6. Viscosity versus shear rate of pastes prepared from 55 vol.% aqueous alumina slurry.

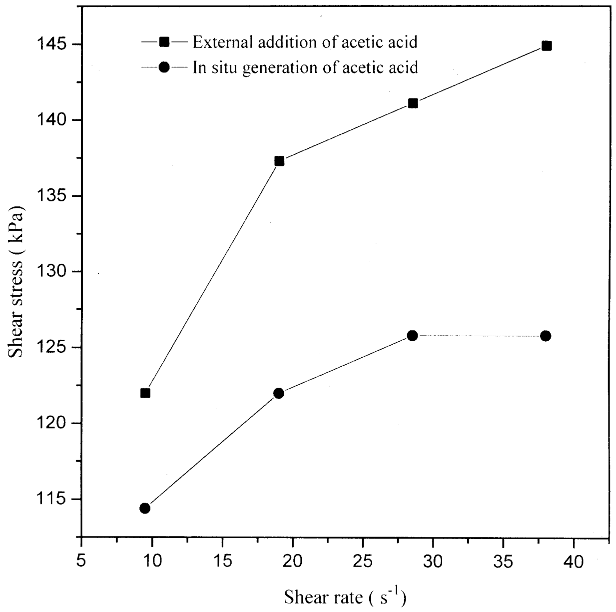

Fig. 7. Shear rate–shear stress plot of pastes prepared from 55 vol.% aqueous alumina slurry.

of acid compared to that of the paste prepared by in situ generation of acid. It was expected that the bridging between particles through the polymer chains by hydrogen bonding would deformed and induced flow to the paste under shear and reform when the shearing force is removed. This characteristics would enable the extrusion of the pastes under low pressure. The alumina tubes extruded by using the pastes prepared by this process showed good surface finish. However, many attempts showed the deformation of the extruded tubes while handling. The extruded samples also developed cracks during drying. The incorporation of 1% PVA in the slurry resulted in alumina pastes with good extrudable consistency and also provided good handling strength and dimensional stability during drying. The green density of the extruded tubes after drying under 65% relative humidity was around 57% TD. The tubes on sintering at 1500°C resulted in sintered density of 97% TD. Fig. 8 shows the photograph of sintered tubes prepared by this method. The shorter one are fragments of tube extruded without PVA binder and the longer one are obtained using 1% PVA. Fig. 9 shows the typical microstructure of the alumina tubes prepared by this technique.

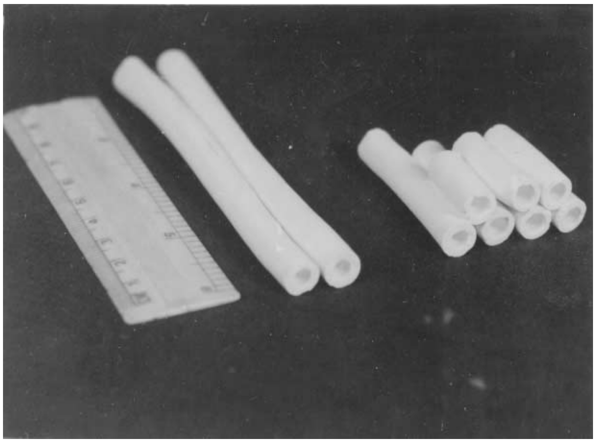

Fig. 8. Photograph of sintered alumina tubes processed by coagulated paste extrusion (shorter tubes — without binder, longer tubes — with 1 wt% PVA binder).

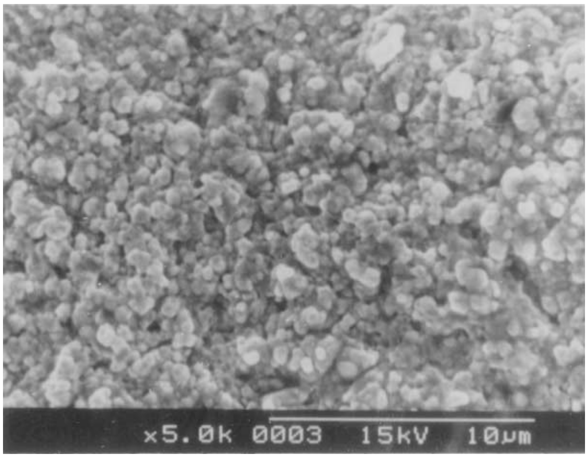

Fig. 9. Fractograph of sintered alumina tube processed through coagulated paste extrusion.

4. Conclusions

The present work successfully demonstrated the preparation of concentrated (55 vol.%) extrudable alumina paste by coagulation of electrosterically stabilised aqueous alumina slurries by in situ generation of acid. Acetic anhydride was used as the source of acid and polyethylene glycol was used to improve the miscibility of acetic anhydride with water. This provides homogeneous gelation of slurry and resulted in a extrudable stiff alumina paste. The addition of acetic anhydride below room temperature showed extended time of gelation and the acid concentration of 0.16 mol/l was found to be minimum. Rheological characteristics indicates that the in situ generation of acid resulted in low viscosity of alumina pastes compared to that of external addition of acid. Incorporation of 1% PVA in the slurry provides additional strength to the extruded tubes against deformation and development of drying cracks. The extruded tubes showed green density of 57% TD and sintered density of 97% TD at 1500°C with fine grained microstructure.

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