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Rheology and packing characteristics of alumina extrusion using boehmite gel as a binder

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Abstract

The present work reports the extrusion characteristics of alumina pastes involving boehmite gel as a binder. Submicron sized alumina (average particle size 0.35 μm) is dispersed in boehmite sol and converted to form a thick alumina paste by controlled flocculation and centrifugation. The paste is further subjected to extrusion for fabricating alumina shapes such as rods and tubes. The paste rheology, workability, green strength and sintered properties are studied and reported. The paste rheology was studied by torque rheometer and the results on the development of torque, viscosity and the yield stress are presented. The alumina paste containing 18 vol.% boehmite binder resulted in 53.4 vol.% solids loading with suitable consistency for low pressure extrusion. The system exhibits a low torque value of 51.85 KPa at shear rate 28.5 s^{-1} and showed plastic behavior. The apparent viscosity of the system showed a shear dependent flow behavior. Alumina–18 vol.% boehmite resulted in a theoretical green density value of 61.4% and a green strength of about 1.05 N/mm^2 on extrusion. The extruded alumina on sintering has a theoretical sintered density of about 98% at 1500°C. The microstructure of sintered alumina showed an average grain size approx. 2 μm. The combination of colloidal processing and gel assisted extrusion yields highly dense, fine grained ceramics. Boehmite ge1 as a binder has advantages such as matrix compatibility, good workability and better green strength.

Keywords: A. Extrusion; D. Alumina; Boehmite; Gel binder; Rheology

1. Introduction

Extrusion is one of the recognized techniques for producing objects of constant cross section with high symmetry such as rods, tubes, honeycomb structures and channels. These products find applications as furnace tubes, membrane supports, particulate filters and heat exchanger tubes and thermocouple sleeves [1–3]. Conventionally, large amounts of polymer binders and organic additives are employed to impart suitable flow properties and wet strength for extrusion. Binders such as methyl cellulose, poly ethylene oxide (hot extrusion), poly vinyl alcohol (PVA), corboxy methyl cellulose and alginates are commonly used. Numerous studies have been reported for their burnout behavior, rheology and green strength [4–6]. There exist a few practical difficulties such as the uniform dispersion of particulate powder into viscous binder, distribution of moisture uniformly throughout the matrix and the elimination of hard agglomerates. The homogeneous mixing of these binders with the matrix is achieved by high intensity mixture, in which the problem of contamination arises. Further, the polymeric binders form micro/macro pores and cracks if they are not burnout properly. An excellent review was published by Evans and Edrisinghe which discussed the key problems associated with ceramic extrusion [7,8]. Colloidal processing is one of the recognized technique for forming suspensions with high solids loading. The agglomerates present in the raw material could break down during the initial stage processing itself in addition to the uniform dispersion of binder phase so that the microstructural heterogeneity can be minimized.

Earlier reports indicated the use of inorganic materials such as sodium silicate, hydrated alumino silicates and clay minerals like montmorillonite as binders for the extrusion process [9]. However, these are not advisable for hi-tech ceramics, where the purity plays an important role over the sintered microstructure. It has been suggested that the very finely divided oxides and hydroxides produced by sol–gel techniques have binding

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characteristics and may be treated as colloidal binders. In particular, a strong analogy between clay gels and sol–gel derived alumimium monohydroxide (Boehmite) has been noted. Boehmite has another advantage in that it gets converted into a stable α-alumina at high temperature, which is already the matrix [10]. It also produces finely sintered alumina grains and considerably increases the mechanical strength of the matrix. Bruno Kindl has used boehmite sol as dispersant for alumina ceramics and reported that the intermediate phases of boehmite increases the densification characteristics [11]. Chen and Cawley reported the use of monohydroxy aluminium oxide as binder along with 0.5% PVA [12]. Sunilkumar et al. studied the behaviour of seeded boehmite gel as an extrusion aid for alumina ceramics and found that the γ-alumina seeded alumina–boehmite mixture have good sintering properties and high mechanical strength [13]. Messing et al. reported seeded boehmite mixed with coarse alumina particles produced porous alumina ceramics [14]. Warrier et al. used boehmite sol as a dispersant for slurry compaction of alumina ceramics [15]. The use of precursor gels for extrusion has definite advantages compared with the conventional polymer–ceramic extrusion. For example, this processing route avoids mechanical mixing steps and associated pick up of contamination from processing equipment [16]. It is also possible to extrude gel without the use of binders and plasticizers, which are necessary for conventional processing, and in many situations this will produce acceptable product quality [17].

The present work is to show the fabrication of high dense alumina shapes through low pressure extrusion using boehmite gel as a binder. The influence of boehmite gel binder on rheological characteristics of alumina and its packing has been presented. The alumina solids loading in presence of boehmite, the development of torque, viscosity and fluidity are studied and presented. The results on green strength, green density are also reported in addition to the sintered density and microstructural features.

2. Experimental

A16 SG alumina (ACC-ALCOA Chemicals, Calcutta) with 99.8% purity, BET surface area of 8–11 m^2/g and an average particle size in the range of 0.3–0.6 μm was used as starting material. Boehmite (Condea Chemicals, Germany) having a surface area of 230 m^2/g was used as binder. Boehmite sol was prepared by dispersing the powder in aqueous medium under vigorous stirring and the stability was controlled by adjusting the pH <3.0 using dilute HNO_3. Alumina was dispersed in boehmite sol under ultrasonic mixing followed by ball milling for 4 h to break up the agglomeration, if any. The slurry concentration of the alumina–boehmite suspension was about 20 vol.%. The resultant suspension was flocculated by the addition of 10% NH_4OH and finally the slurry was centrifuged to remove the excess water and a thick paste was obtained. Moisture analysis was carried out at 90°C to find the critical amount of moisture needed for extrusion. Rheological characteristics of alumina pastes with and without boehmite binder was studied by Torque rheometer (Brabender plasticorder, Model PLE 651) at room temperature. The development of torque was observed by changing the rotor speed in the range 10–40 rpm using a measuring mixer W 50. The apparent viscosity was calculated by dividing the torque with rotor speed.

2.1. Extrusion procedures

The laboratory model vertically mounted plunger type extruder was used in this study and schematically represented in Fig. 1. Extruder assembly is made of stainless steel and has an anti corrosive coating inside. The feed chamber was 1 in. in diameter and 6 in. in length. The barrel and die was lubricated with stearic acid. The conical die arrangement having an entrance angle of 45° and inner diameter of 6 mm was used as the nozzle. The alumina paste was fed into the extruder chamber and the pressure was carefully applied through the plunger at a rate of 2 mm/min. Alumina rods having 6-mm diameter and 150-mm length was extruded. Similarly tubes with inner diameter 2-mm and outer diameter 6 mm was extruded. The green rods and tubes were dried in humidity controlled oven (REMI Environment chamber, India) at 65% relative humidity and 45°C for 48 h. Linear drying shrinkage and green density was calculated from dimensional measurements. Green strength was determined by diametrical compression testing at a rate of 1 mm/min (INSTRON, Model 1011). The L/D ratio of the discs obtained from

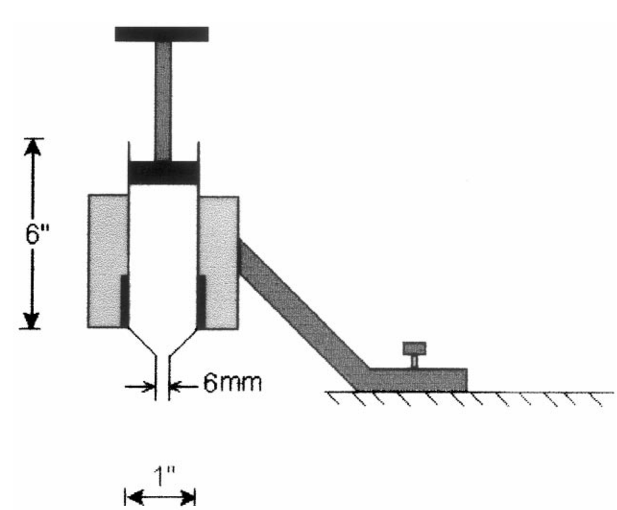


Fig. 1. Schematic sketch of laboratory extruder.

the extruded rods was fixed at 4. Sintering of extruded rods and tubes were carried out in the temperature range 1350–1500°C for 2 h using high temperature programmable furnace (Nabertherm, Germany) with initial heating rate of 5°C/min up to 1000°C and 8°C up to 1250°C and 3°C up to the final sintering temperatures. At this heating rate no problem with binder burnout was observed. Sintered density was measured by Archimedes principle. Sintered microstructure was observed on a fractured surface (SEM, Hitachi, Model 2420, Japan).

3. Results and discussions

3.1. Effect of boehmite on paste rheology

Fig. 2 shows the moisture analysis of alumina–boehmite pastes obtained through controlled flocculation and centrifugation. The paste as prepared has a total moisture content of about 34%. At this semi-fluid condition the boehmite gels may have excellent workability but cannot hold the particles to perform as a binder. The controlled drying at 90°C for about 70–100 min reduce the moisture level to 24%, which yielded suitable consistency for extrusion. At this level, a good shape retaining capacity, and a smooth extruded surface was observed. The drying of pastes between 75 and 90 min also resulted in alumina solids loading in the range of 52 vol.%. Boehmite is the monohydrate of alumina [AlOOH] and has a layered structure, bonded by weak hydrogen bonds. The controlled flocculation followed by careful drying yields gelatinous boehmite with binding efficiency. These two factors control the interactions of alumina–nano size boehmite in aqueous medium and alter the inter particle potential and the extent of adhesive nature to strengthen the gel network. The flocculation around pH 5.5–6.2 is found to be optimum for producing boehmite gel that has reasonable gel strength to behave as binder. The flocculation beyond this range may also result in compacts but it has poor green strength and was very weak for further handling. Fig. 3 shows the development of torque for alumina pastes at various levels of boehmite binder. The alumina without boehmite showed a higher torque value of 69.8 KPa even at low shear rate of 9.5 s^{-1}, which gradually increases with increase in shear rates. The incorporation of boehmite binder initially resulted in higher torque range and on subsequent addition the torque was minimised to an acceptable level. The total torque calculated for alumina–6 vol.% boehmite was about 95 KPa at a low shear rate of 9.5 s^{-1} and 130 KPa at a shear rate of 28.5 s^{-1}. It remains without change even if the shear rate was increased to 38 s^{-1}. However, on further addition of boehmite, the torque was considerably decreased and a low torque was maintained even at high shear rates. Particularly, the alumina containing 18 vol.%

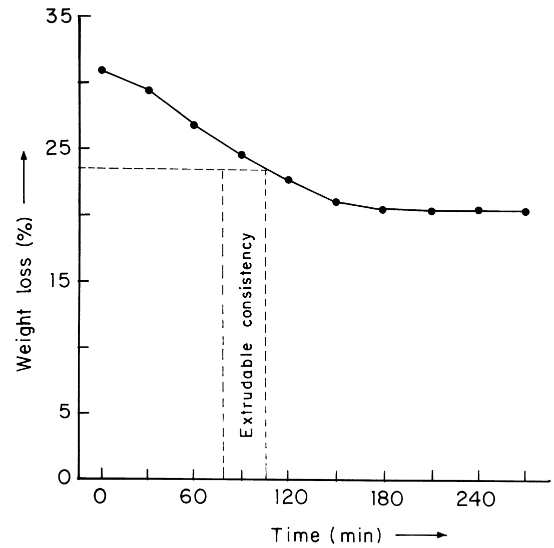


Fig. 2. Moisture analysis of alumina–boehmite paste.

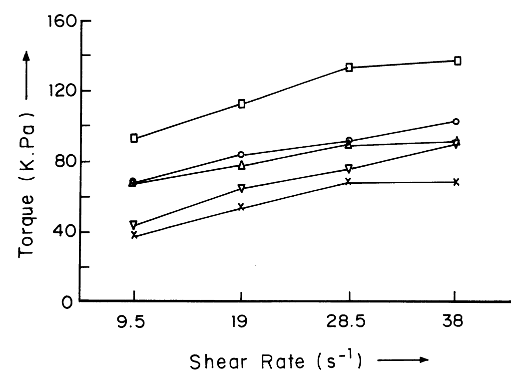


Fig. 3. Torque rheology of alumina paste at different levels of boehmite. (◆) Alumina, (□) 5% AlOOH, (▲) 10% AlOOH, (×) 15% AlOOH, (∗) 20% AlOOH.

boehmite resulted in low torque value of less than 40 KPa at shear rate of 9.5 s^{-1} and 51.8 KPa at shear rate of 28.5 s^{-1}. In all the cases, it was observed that the initial torque at low shear of 9.5 s^{-1}, gradually increases up to the shear rate of 28.5 s^{-1} and remains without any change up to a shear rate of 38 s^{-1}. In general, the alumina–boehmite system showed Bingham plastic flow behaviour, which is one of the essential factors for extrusion process. It was noted that for the higher addition of boehmite, i.e. above 18 vol.%, the torque is gradually increasing. It is well known that boehmite is hydrophilic in nature, the hydrated layer develops over boehmite surfaces [18]. Since boehmite is extremely fine, it gets adsorbed over the alumina surfaces. When the gelation of boehmite occurs at controlled pH conditions, a weakly flocculated state of alumina–boehmite exists, where a long range attractive inter particle Van der Waals forces and a short range repulsive hydration forces are present, which ultimately decreases the frictional forces and increases the degree of plasticity and reduce the torque [19]. However, with increase in boehmite, the binder phase segregation associated with agglomeration may takes place, resulting in increased torque [20]. Fig. 4 is the yield stress value of alumina pastes at various boehmite levels calculated from the plot of square root of shear rate against the square root of torque. The yield stress was obtained by extrapolating the straight-line towards the torque axis. The alumina without boehmite has very high yield stress, i.e. 65 KPa and gradually decreasing with the addition of boehmite. Alumina–18 vol.% of boehmite showed a very low yield stress value of about 36.1 KPa. The slope of the curve was calculated to be < 1.0, which also indicates the degree of plasticity of the ceramic mass. Fig. 5 is the apparent viscosity [η] of alumina paste with respect to the addition of boehmite binder. A shear dependent flow profile is generally observed, which is characterized as 'shear thinning' flow behaviour.

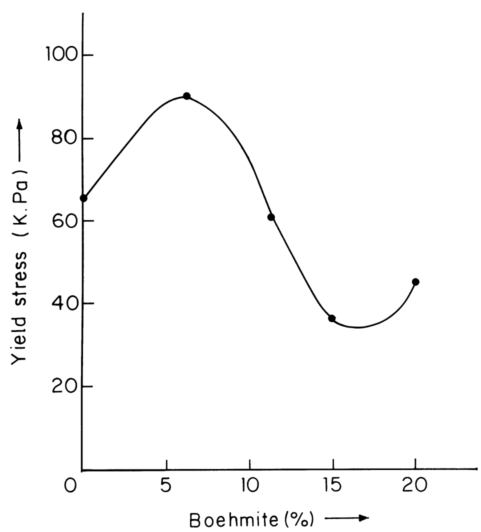


Fig. 4. Yield stress curve of alumina–boehmite paste.

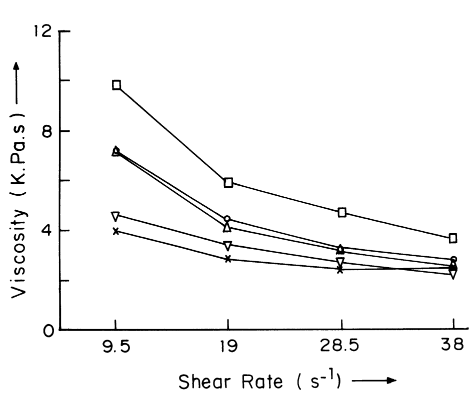


Fig. 5. Viscosity patterns of alumina–boehmite paste. (◆) Alumina, (□) 5% AlOOH, (▲) 10% AlOOH, (×) 15% AlOOH, (∗) 20% AlOOH.

3.2. *Effect of boehmite on alumina solids loading*

Fig. 6(a) and (b) shows the influence of alumina solids loading in presence of boehmite. The alumina without boehmite shows a reasonably low torque up to 51.45 vol.% of solids at shear rates in the range of 10–30 rpm. The increase in solids loading to 53.45 vol.% resulted in very high torque, i.e. in the range of 80–120 KPa. However, the presence of boehmite influences the torque considerably for a given solids loading. The alumina consisting 18 vol.% of boehmite resulted in 54 vol.% of solids in which a total torque is in the range less than 80 KPa. This may be due to the adsorption of boehmite particles over alumina surface, which modifies the surface characteristics. It is already reported that the presence of bi-modal particle size distribution with alumina controls the surface forces and increases the total solids loading [21]. This is further clear from the Fig. 7 in which the fluidity of alumina–boehmite is presented with respect to solids loading. The alumina without boehmite showed an increased fluidity only when the solids loading is decreased. Whereas, the boehmite incorporated alumina exhibit reasonable fluidity even when the solids loading is increased. It is evident that the boehmite not only acts as a binder, but also behaves as a plasticizer.

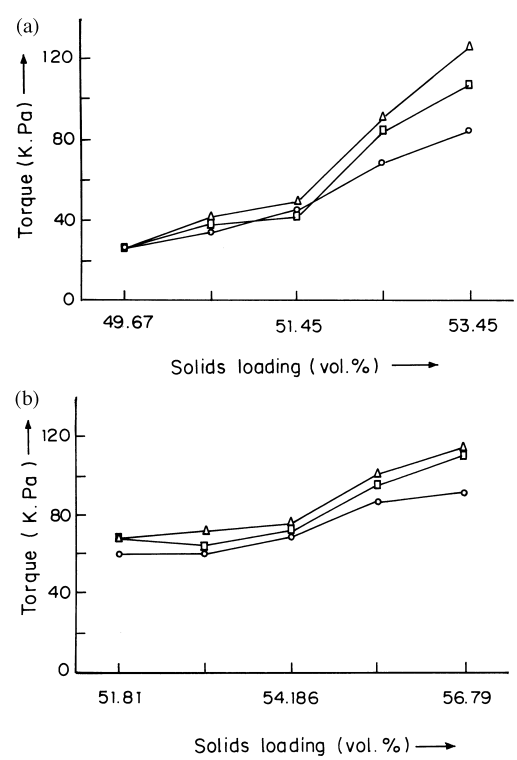


Fig. 6. (a) Torque rheology of alumina at different solids loading. (◆) 10 RPM, (□) 20 RPM, (▲) 30 RPM. (b) Torque rheology of alumina–boehmite paste at different solids loading. (◆ 10 RPM, (□) 20 RPM, (▲) 30 RPM.

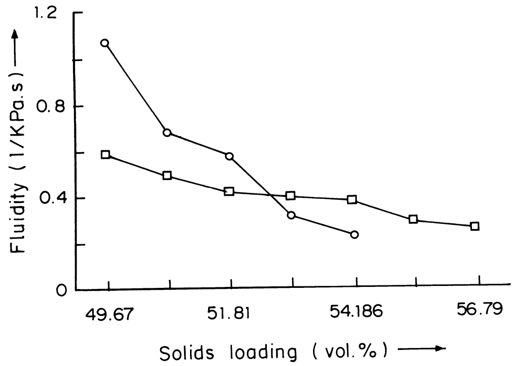


Fig. 7. Fluidity pattern of alumina with and without boehmite. (◆) without boehmite, (□) with boehmite.

3.3. Packing characteristics of alumina at different boehmite content

The packing characteristics can be understood from the green density measurements presented in Fig. 8. Alumina without binder has green density only about 51.6% TD and is increased with increasing boehmite content. The maximum theoretical green density of about 61.4% is observed for samples having 18 vol.% boehmite. This decreases when the amount of boehmite is increased further. It is known that during extrusion process, ceramic paste is subjected to various deformations and complex shear occurs during mass flow of concentrated suspension. Normally, it is the binder, which controls the extent of shear and maintains the consistency of the powder mass throughout the cross section of the die. However, the presence of excess binder, results in higher shear that limits the flow characteristics of powder mass and lower the packing efficiency [22]. The boehmite concentration up to 18 vol.% is found to be suitable to maintain the flow property and to yield optimum fluidity for alumina pastes. At this range, possibly, the cohesiveness of boehmite–alumina increases and result in higher packing and green density [23]. Fig. 9 shows the green strength values of extruded alumina using boehmite. The alumina containing 18 vol.% boehmite showed 1.05 N/mm^2 strength. The maximum

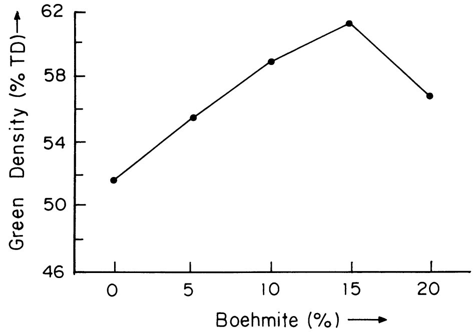


Fig. 8. Green density (%TD) of extruded alumina.

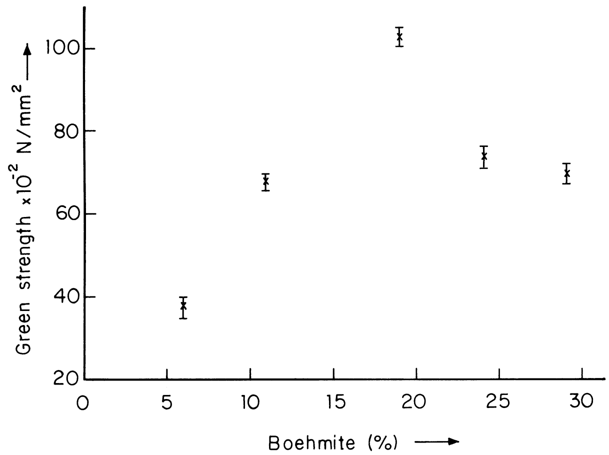


Fig. 9. Diametrical green strength of extruded alumina.

linear shrinkage of extruded alumina after drying at 45°C, relative humidity 65% is only <3%. This further showed that the boehmite could be used as binders for near net shaping of ceramic shapes.

3.4. Sintering characteristics

The sintered density of extruded alumina containing different amounts of boehmite content in the sintering temperature range 1300–1500°C is presented in Fig. 10. The alumina–boehmite extruded samples generally showing sintered density above 90% TD. The alumina containing 18 vol.% boehmite has a sintered density of about 96.6% TD at 1450°C, which further increased to 98.2% theoretical value at 1550°C. One of the reasons for this increased densification is the formation of intermediate phases derived from the thermal decomposition of boehmite. The boehmite during heat treatment produces γ-alumina phase at around 450°C, which remains up to 800°C. This is already reported to be a more active phase. This may also yield additional nucleating sites during the initial stage of sintering and resulted in increased densification. Fig. 11 shows the

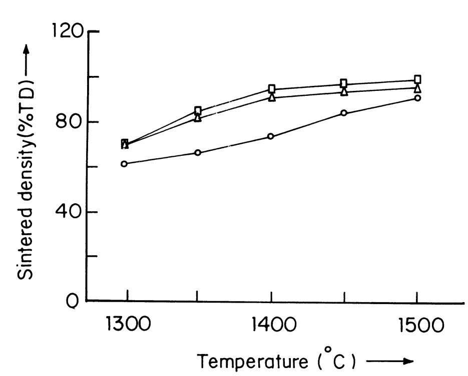
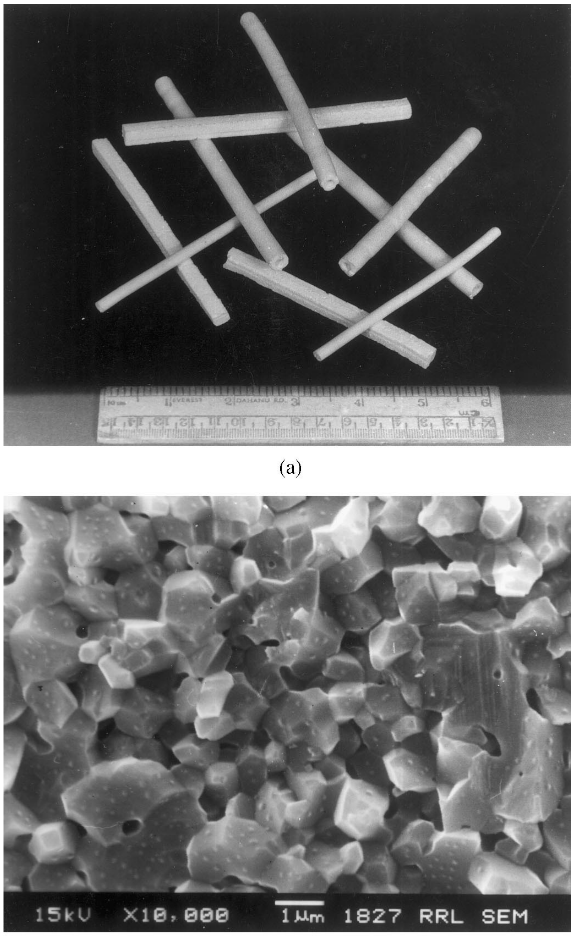


Fig. 10. Sintered density (%TD) of extruded alumina. (◆) Alumina, (□) Alumina–18 vol.% boehmite, (▲) Alumina–24 vol.% boehmite.



(a)

(b)

Fig. 11. Alumina shapes and the fractograph of sintered alumina.

sintered rods and tubes fabricated by this method and also a fractograph of sintered alumina obtained through gel assisted extrusion. It shows grains on the order of 1.0 µm in size which are derived out of boehmite and also grains on the order of 2–3 µm, which are derived from basic alumina. However, such microstructure is favourable because it increases the number of sintered fine grains in the matrix, which may ultimately improve the mechanical strength of the ceramic. There are also some isolated closed pores present in the sintered material.

4. Conclusion

Highly dense, medium length alumina rods and tubes were fabricated using paste extrusion technique. The role of conventional binders and the use of organic vehicle is completely avoided and inorganic particulate gel assisted ceramic extrusion is attempted. The boehmite particulate sol was used for alumina dispersion and partly flocculated boehmite gel at pH 6.7 found favourable to be used as binder for alumina ceramic extrusion. The boehmite gel binder up to 18 vol.% yields very low torque and viscosity and imparts suitable flow property for extrusion. The maximum green density of about 61.4% TD was achieved with only 3.0% linear drying shrinkage. The sintered alumina has sintered density of about 98.2% TD at 1550°C. The sintered microstructure showed uniformly distributed, extremely fine grains around the bulk alumina grains having size of about < 2 µm. The boehmite gel not only provides excellent green strength but also acts as sintering aid for alumina ceramics.

References

[1] P.M. Eggerstedt, J.F. Zievers, E.C. Zievers, Choose the right ceramic for filtering hot gases, Chemical Engineering Progress 1 (1993) 62–68.

[2] H.T. Wang, X.Q. Liu, Y. Zhou, D.K. Peng, G.Y. Meng, Preparation and characterization of porous ceramic supports, Membrane Science Technology 17 (1997) 47–52.

[3] A.J. Keizer, A.J. Burgraff, Porous ceramic materials in membrane applications, Scientific Ceramics 39 (1998) 213–221.

[4] J.E. Scheutz, Methyl cellulose polymers as binders for extrusion of ceramics, Journal of the American Ceramic Society 88 (1986) 1556–1559.

[5] M.J. Cima, M. Dudziak, J.A. Lewis, Observation of poly(vinyl butyral)–dibutyl phthalate binder capillary migration, Journal of the American Ceramic Society 72 (1989) 1087–1090.

[6] T. Zhang, S. Blackburn, J. Bridgewater, Properties of ceramics suspensions for injection molding based on agar binder, British Ceramic Transactions 93 (1994) 229–233.

[7] M.J. Edirisinghe, J.R.G. Evans, Review: fabrication of engineering ceramics by injection molding: I Materials selection, International Journal of High Tech. Ceramics 2 (1986) 1–31.

[8] M.J. Edirisinghe, J.R.G. Evans, Review: fabrication of engineering ceramics by injection moulding: II Techniques, International Journal of High Tech. Ceramics 2 (1986) 249–278.

[9] M. Miller, R.A. Haber, The use of montmorillonite as extrusion aids for alumina, Ceramic Engineering Science Proceedings 12 (1991) 13–48.

[10] T.V. Mani, P. Krishnapillai, A.D. Damodaran, K.G.K. Warrier, Dependence of calcination conditions of boehmite particulate characteristics and sinteability, Materials Letters 19 (1994) 237–241.

[11] B. Kindl, D.J. Carlsson, V. Deslandes, A.J. Hoddenbagh, Preparation of α-alumina ceramics: the use of boehmite sol as dispersion agent, Ceramics International 17 (1991) 347–350.

[12] A.Y. Chen, J.D. Cawley, Extrusion of α-alumina boehimte mixtures, Journal of the American Ceramic Society 75 (3) (1991) 575–579.

[13] C. Sunilkumar, U.S. Hareesh, A.D. Damodaran, K.G.K. Warrier, Monohydroxy aluminium oxide as a reactive binder for extrusion of alumina ceramics, Journal of the European Ceramic Society 17 (1997) 1167–1172.

[14] S. Kwon, G.L. Messing, Constrained densification in boehmite–alumina mixtures for the fabrication of porous alumina ceramics, Journal of Materials Science 33 (1998) 913–921.

[15] S. Ananthakumar, Vijay Raja, K.G.K. Warrier, Effect of nanoparticulate boehmite sol as dispersant for slurry compaction of alumina ceramics, Materials Letters 43 (2000) 174–179.

[16] H. Bohm, S. Blackburn, Effect of mixing procedures on fine alumina paste extrusion, British Ceramic Transactions 93 (5) (1994) 169–177.

[17] P. Kilbride, A.J. Barker, Enhanced densification by seeding of extruded boehmite gels derived by hydrothermal decomposition of basic aluminium acetate, British Ceramic Transactions 93 (5) (1994) 187–191.

[18] C. Pierre, D.R. Uhlmann, Gelation of aluminium hydroxide sols, Journal of the American Ceramic Society 70 (10) (1987) 28–32.

[19] H. Schilling, R.A. Bellman, R.N. Smith, H. Goel, Plasticizing aqueous suspensions of concentrated alumina with maltodextrin sugar, Journal of the American Ceramic Society 18 (12) (1998) 57–66.

[20] R.J. Huzzard, S. Blackburn, Influence of solids loading on aqueous injection molding paste, British Ceramic Transactions 98 (2) (1999) 49–56.

[21] J.H. Song, J.R.G. Evans, Ultrafine ceramic powder injection moulding — the role of dispersants, Journal of Rheology 40 (1) (1996) 131–152.

[22] J. Graczyk, W. Gleissle, Rheology and extrudability of alumina paste for catalysis, Industrial Ceramics 16 (3) (1996) 199–203.

[23] B.V. Velamakanni, F.F. Lange, Effect of interparticle potentials and sedimentation on particle packing density of bimodal distribution during pressure filtration, Journal of the American Ceramic Society 74 (1) (1994) 166–172.