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Effect of boehmite and organic binders on extrusion of alumina

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Abstract

The extrusion of alumina pastes processed by sol gel assisted colloidal processing involving nano particulate boehmite gel as binder phase was studied. Submicron alumina was dispersed in aqueous boehmite sol at pH 3 followed by gelation and centrifugal filtration to form alumina–boehmite pastes and further subjected to single screw ceramic extrusion. Alumina–15 wt.% boehmite pastes exerted a peak pressure of 1.6 MPa at the die exit at a screw speed of 20 rpm. The pressure analysis of alumina–boehmite paste was compared with the conventional water-soluble HPMC polymer system. The exit pressure for alumina–HPMC system was only 0.2 MPa. The addition of processing aids such as 0.25 wt.% of PVA, 3.0 wt.% of either PEG or glycerin with alumina–15 wt.% boehmite paste exhibit very low exit pressure as equal to that of the HPMC binder. A green density of 65% theoretical was achieved for extruded alumina. The alumina rods attained 98% theoretical sintered density at 1500 °C. The study shows the use of nano particulate boehmite gel as binder for alumina ceramics as well as the influence of conventional ceramic processing additives on extrusion characteristics of alumina–boehmite pastes.

Keywords: A. Sol–gel processes; A. Extrusion; D. Alumina; Boehmite; Colloidal processing; Processing additives

1. Introduction

Extrusion of advanced ceramic parts using conventional polymer binders poses technical challenges such us high degree of powder-polymer mixing, great control over dimensional accuracy and binder burnout, formation of micro cracks and pores and poor mechanical strength [1]. Extrusion of alumina for the fabrication of membrane supports, porous filters, thread guides, sleeves and valves are expected to have high reliability and improved performance [2,3]. Alumina is a known non-plastic material and therefore the extrusion of alumina pastes requires processing additives such as binders, dispersants, plasticizers and lubricating agents, to impart plasticity and flow characteristics. Aqueous extrusion of ceramic pastes prepared with water-soluble polymer binders such as hydroxyl propyl methyl cellulose (HPMC), hydroxyl ethyl cellulose, maltodextrin, agar, agarose, alginate and carbohydrate have been reported and proved to be more viable [4–8]. The extrusion characteristics of ceramic pastes such as the powder packing, rheology and pressure development in both the conventional polymers and water-soluble polymer binders have also been well studied and reported widely in the literature [9,10]. Recently, it has been suggested that the addition of very fine particles, preferably in nano size range, controls the surface properties of micron sized powder particles and imparts necessary plasticity suitable for extrusion [11]. Sol gel assisted colloidal processing is one of the promising techniques for the preparation ceramic pastes with nano scale fine particles. The advantages over this method are increased wetting of powder surface, accurate control over desired moisture level, elimination of agglomeration and contamination.

Nano particulate boehmite has already been used for alumina and the extrusion of alumina–boehmite mixtures are reported earlier. The advantages mentioned are good compatibility with the matrix, elimination of binder burn out unit process, non-contamination of ceramic mass with metal parts, and fast sintering. Boehmite sol is also realized as a good dispersant for alumina powders [12,13]. The formations of intermediate phases like γ- alumina during the heat treatment of boehmite promote the sintering kinetics of alumina, and control the microstructure of the sintered ceramic. Sunilkumar et al. used seeded boehmite gel as an

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extrusion aid for alumina and alumina–zirconia ceramics [14]. Kwon and Messing used seeded boehmite mixed with coarse alumina particles to produce porous alumina ceramics with good mechanical strength [15]. More recently, the rheology, packing and the sintering characteristics of alumina–boehmite mixture have also been reported [16]. However, a systematic study on the influence of boehmite on pressure development and plasticity during extrusion has not been reported.

In the present work, single screw extrusion of alumina–boehmite pastes was studied and issues related to the development of pressure, alumina packing and rheology are reported. Processing additives such as paste modifiers were also studied and reported in addition to the sintering characteristics and microstructural features.

2. Experimental

A16 SG alumina (ACC-ALCOA Chemicals, Kolkatta) with 99.8% purity, BET surface area 8–11 m^2/g and the average particle size 0.3 μm and boehmite (Condea Chemicals, Germany) having surface area 230 m^2/g were used. Reagent grade polyethylene glycol (average molecular weight 285–315, s.d. Fine Chemicals Pvt. Ltd., India) glycerin (average molecular weight 92.10, s.d. Fine Chemicals Pvt. Ltd.) and polyvinyl alcohol (PVA; molecular weight 49,000, Fluka Chemicals, Switzerland) were used as processing additives. Hydroxy propyl methyl cellulose (average molecular weight 12,000, Wilson Laboratories, India) was also used as polymer binder and alumina–8 wt.% HPMC paste was subjected to extrusion for comparison.

Sol–gel assisted colloidal processing of alumina–boehmite pastes for the extrusion was carried out by the following procedure. The alumina pastes consisting of boehmite binder in the range 15–40 wt.% were prepared. In each set of alumina–boehmite pastes, total weight of 120 g was fixed as basis. Accordingly, the required amount of alumina and boehmite was calculated. In a typical experiment, the calculated alumina was dispersed in boehmite sol, which was first obtained by dispersing the boehmite powder in an aqueous medium. The boehmite concentration was maintained at 5 wt.% for producing a stable sol. The pH of the suspension was adjusted to 3.0 by adding dilute nitric acid. The slurry was stirred vigorously and ball milled for about 3 h. The suspension was flocculated at pH 6.5 by the addition of dilute ammonium hydroxide. The flocculated alumina–boehmite suspension was aged for 12 h and excess water was removed by centrifugal filtration to form a thick alumina paste. The total solids loading in alumina–boehmite paste was estimated as 58 vol%. The paste was kept overnight before subjecting to extrusion. The procedure was repeated for preparing alumina pastes with varying amounts of boehmite. The extrusion was carried out using Dr. Collin's single screw ceramic extruder (Dr. Collins GmbH, Germany).

The screw has the diameter $D = 30$ mm and length $L = 10 \times D$. The alumina paste was fed into the barrel in the form of mini spheres having approximate size 5 mm diameter with the help of a feed roller running at a constant speed of 15 rpm. The screw speed was fixed at 20 rpm. These parameters were fixed by performing many trials before starting the experiments. The development of pressure at the die exit was monitored with a standard pressure transducer (DYN R4-1/2-6C-7.6) and the pressure curves were recorded. Alumina rods having 10 mm diameter and 15 cm length were extruded. The viscosity and torque was studied by plasticorder equipment (Brabender, Model PLE 651) at room temperature at different shear rates using a measuring mixer head W 50. The green rods were dried in a humidity controlled oven (REMI Environment Chamber, India) at 65% RH and 45 °C for 48 h. Linear drying shrinkage was calculated from dimensional measurements. The green extruded rods after drying were sintered in the temperature range 1300–1500 °C for 2 h using a high-temperature furnace (Nabertherm, Germany) with initial heating rate of 5 °C/min up to 1000 °C and 8 °C/min up to 1250 °C and 3 °C/min up to the final sintering temperatures. Sintered density was measured by Archimedes' principle. Sintered microstructure was observed on a fractured surface using a scanning electron microscope (Hitachi-2420, Japan). The green extruded alumina rod was machined using high-speed mechanical lathe.

3. Results

3.1. Extrusion characteristics of alumina–boehmite pastes

Fig. 1 shows the peak exit pressures for alumina–8 wt.% HPMC and alumina–boehmite pastes (15–40 wt.%) developed at the die entrance for the given duration of the extrusion process. The alumina paste containing conventional HPMC binder system showed remarkably low exit pressure when compared to alumina–boehmite pastes. The maximum exit pressure determined for alumina–HPMC system was only 0.2 MPa. On the other hand, the alumina–boehmite pastes showed higher level of peak exit pressures for all the sample batches for the same extrusion conditions. However, the maximum pressure exerted by the alumina–boehmite pastes containing up to 20 wt.% boehmite was low when compared to alumina pastes containing 30 and 40 wt.% of boehmite. The respective peak exit pressures determined for alumina 15 and 20 wt.% of boehmite pastes were 1.6 and 1.2 MPa. The exit pressure was gradually increased with increasing amounts of boehmite. For example, alumina–40 wt.% of boehmite increased the pressure from 1.2 to 2.4 MPa under identical conditions. Fig. 2 shows the effect of the addition of PVA to alumina–boehmite paste. The addition of 0.25 wt.% PVA with alumina–boehmite decreased the exit pressure from 1.6 to 1.0 MPa. However, the paste appeared to be very stiff and paste flow was very difficult.

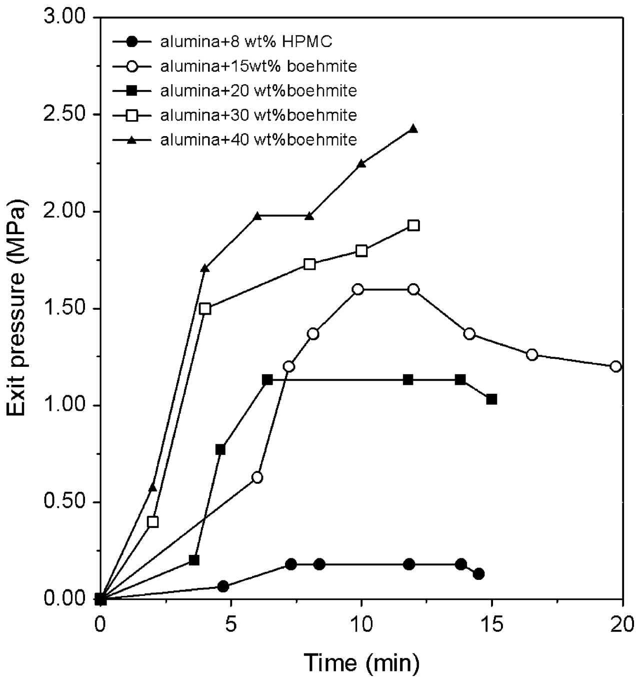

Fig. 1. Development of exit pressures with respect to amount of boehmite binder phase.

Figs. 3 and 4 show the effect of polyethylene glycol and glycerin on pressure generation of alumina–boehmite pastes. The addition of 1 wt.% PEG does not change the pressure level appreciably, but when the addition of PEG is increased to 3 wt.%, the pressure decreased to 0.6 MPa. In the case of glycerin addition, alumina paste yields very low pressure as equal to that of the HPMC binder. It was determined that 3 wt.% glycerin showed the maximum exit pressure only 0.3 MPa. Fig. 5 shows the torque rheology of alumina–boehmite paste with and without additives at different shear rates. The alumina paste without any additives exhibits a torque of 69.8 kPa even at low shear rate of 9.8 s^{-1}. The torque was further increased with increasing shear rates. The incorporation of boehmite up to 15 wt.% lowered the torque appreciably and a very low torque was

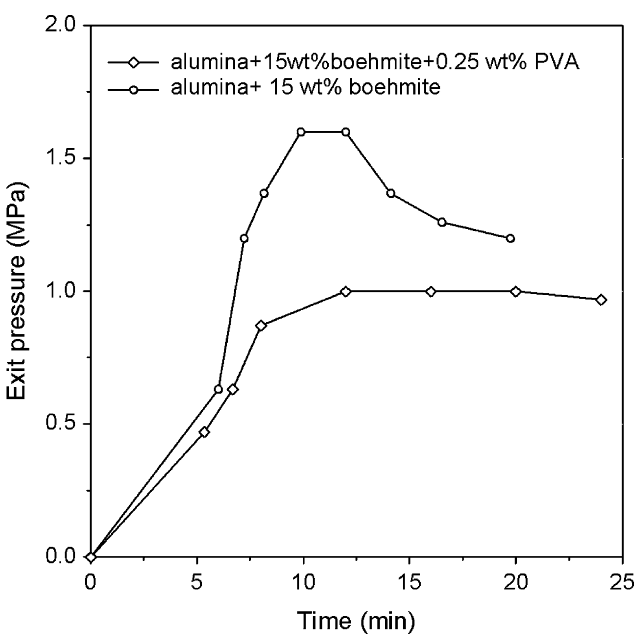

Fig. 2. Effect of PVA addition with alumina–boehmite paste.

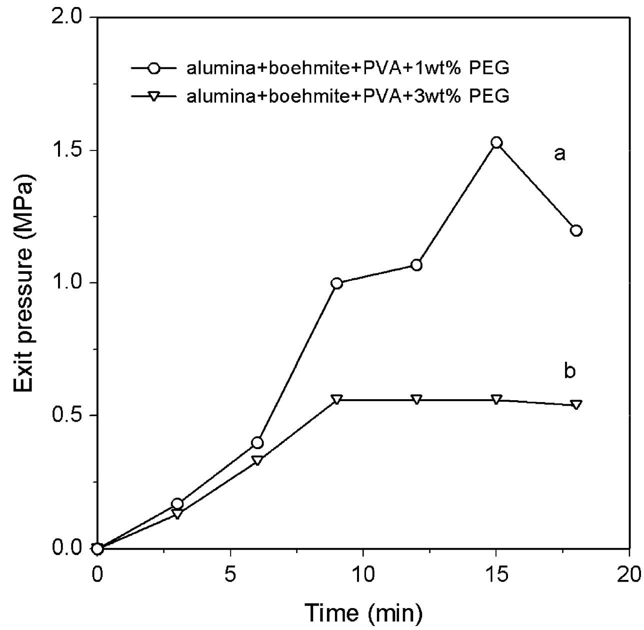

Fig. 3. Effect of the addition of PEG on alumina–boehmite pastes. (a) Alumina + 15 wt.% boehmite + 0.25 wt.% PVA + 1 wt.% PEG. (b) Alumina + 15 wt.% boehmite + 0.25 wt.% PVA + 3 wt.% PEG.

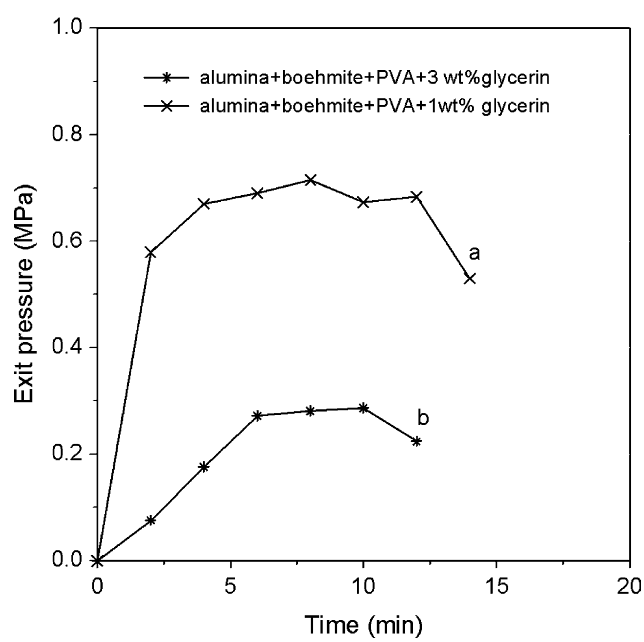

Fig. 4. Effect of glycerin on alumina–boehmite pastes. (a) Alumina + 15 wt.% boehmite + 0.25 wt.% PVA + 1 wt.% glycerin. (b) Alumina + 15 wt.% boehmite + 0.25 wt.% PVA + 3 wt.% glycerin.

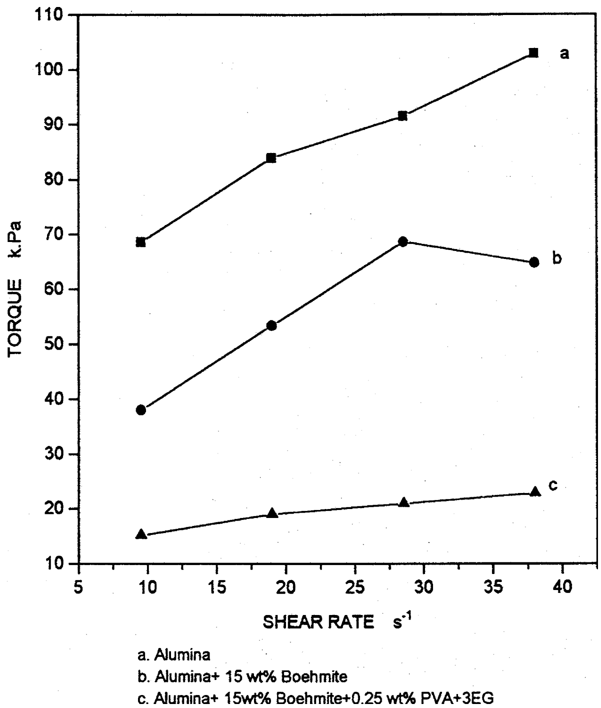

Fig. 5. Torque rheology of alumina–boehmite paste. (a) Without boehmite. (b) With 15 wt.% of boehmite. (c) Alumina+15 wt.% boehmite+0.25 wt.% PVA + 3 wt.% PEG.

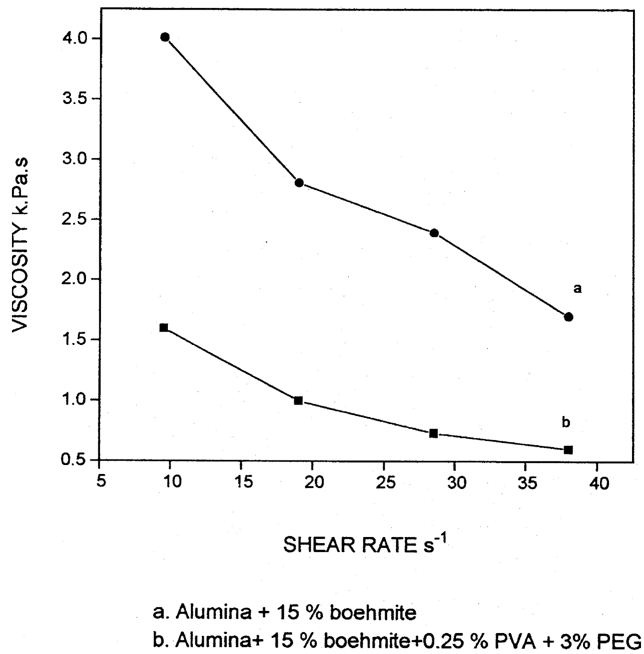

Fig. 6. Viscosity of alumina–boehmite paste. (a) Alumina + 15 wt.% boehmite. (b) Alumina + 15 wt.% boehmite + 0.25 wt.% PVA + 3 wt.% PEG.

observed even at high shear rates. The average torque values of 38 and 50 kPa were measured at a shear rates of 9 and 19 s^{-1} for alumina–15 wt.% of boehmite. The paste in presence of 0.25 wt.% of PVA and 3% of PEG further showed that the torque is lowered from 38 to 15 kPa at shear rate 9.8 s^{-1}. The torque was considerably lower even at high shear rates. The alumina–boehmite paste exhibits 'Bingham' type plastic flow with very low yield stress. Fig. 6 shows the viscosity patterns of alumina–boehmite paste in the presence of the additives. The viscosity decreases with increasing shear rate indicating that the system has shear thinning flow behaviour. The alumina–boehmite paste also resulted in low viscosity in presence of the paste modifiers.

3.2. Physical properties of extruded alumina

The alumina packing during extrusion of alumina–boehmite pastes was quite high and the alumina–15 wt.% boehmite paste in presence of 0.25 wt.% PVA, 3.0% of either polyethylene glycol or glycerin showed 65% theoretical green density during extrusion. The alumina density 3.89 g/cm^3 was used for calculating the theoretical green density. Fig. 7 shows the SEM micrograph of green extruded alumina rod on fractured mode. It is seen that the particle packing is uniform and dense and there are macro voids and micro cracks. The linear drying shrinkage of the extruded alumina rod was only 8%. The extruded alumina also showed high green strength, which was indirectly observed by subjecting the rod for machining under high-speed lathe. The extruded rod has enough strength to bear the working load until a stepwise turning was made. Fig. 8 shows the microstructure of the extruded alumina sintered at 1500 °C. At this temperature, the extruded alumina attained 98% theoretical sintered density. The microstructure of the sintered alumina rod at 1500 °C was dense with an average grain size in the range 2–3 μm. There appears some isolated porosity along the grain boundaries.

3.3. Discussions

During extrusion, the flow of pastes through a narrow die occurs essentially by a combination of plastic deformation

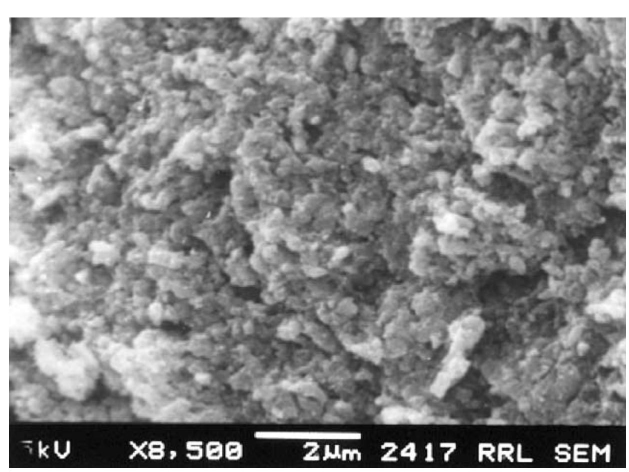

Fig. 7. SEM microstructure of green extruded alumina rod.

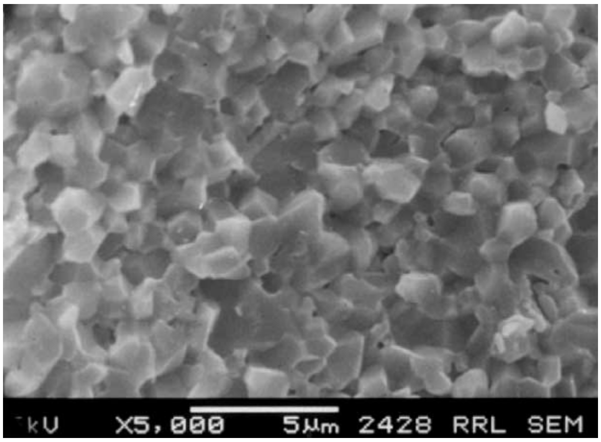

Fig. 8. SEM microstructure of extruded alumina sintered at 1500 °C.

and shearing. It is the viscous binder that controls the stress distribution uniformly throughout the cross sectional area of die land and the entrance [17,18]. The polymer binders exhibit low viscosity even at high shear rates and therefore a very low peak pressure was obtained when HPMC was used. However, in alumina–boehmite system, the phenomenon is different and both physical and chemical effects are possible. The boehmite particles exist on the order of nanosize, which gets adsorbed on the surface of the micrometer sized alumina particles during colloidal treatment under specific pH conditions [19]. On further control of surface charges by flocculating the slurry, the gelation of boehmite takes place. Alumina particles covered with gelated boehmite particles exhibit low viscosity and finally induce plasticity for the paste flow. Boehmite is also known to have a layered structure and during shearing, sliding or slipping occurs and causes flow of pastes [20]. The pressure is low when the binder phase is just adequate to yield the plasticity and it is high if the binder phase exceeded certain limit. It was also reported that the higher volume fraction of fine particles generally have a tendency for agglomeration and also segregation, which may finally affect the plastic flow and therefore resulted in increased pressures [21]. In the case of PVA addition, the strength and viscosity of the boehmite gel network is increased which ultimately make the paste stiffer and resulted in increased pressure. However, such a nature leads to high green strength and therefore additives such as polyethylene glycol (PEG) and glycerin (GLY) were added along with PVA. It is already known that polyethylene glycol and glycerin have relatively high polarity, are highly viscous and are completely miscible in aqueous medium [22,23]. The polyethylene glycol improves the wetting of alumina while the glycerin contributes to retention of moisture and also reduces the friction between particles during flowing to lower the exit pressure [24]. Unlike the case of polymers, where a polymeric bridge controls the packing of powder particles [25,26], here the presence of weak hydration force as well as the adhesive force binds the particles together and retain the shape [27,28]. The bi-modal particle size nature of alumina–boehmite mixture resulted in high degree of alumina packing and high green density and handling strength [29]. It was already reported that the boehmite produces more active intermediate phases during sintering and such phases are facilitates the densification kinetics of alumina and resulted in high sintered density at relatively low temperatures [30].

4. Conclusion

The preparation of alumina–boehmite pastes by sol–gel assisted colloidal processing was performed with and without processing additives and the paste properties during single screw ceramic extrusion was studied and presented. The development of peak exit pressure of alumina–boehmite paste at the die entrance was compared with alumina–HPMC polymer binder. The alumina–HPMC ceramic paste showed the maximum exit pressure only 0.2 MPa. The alumina–boehmite mixture exerted comparatively high peak pressure at the die exit during extrusion and it was determined as 1.6 MPa for alumina–15 wt.% boehmite paste. However, the processing additives such as glycerin and PVA considerably lowered the peak exit pressure. Alumina–15wt.% boehmite pastes in presence of 3 wt.% of either glycerin or poly ethylene glycol and 0.25 wt.% of PVA showed very low exit pressures as equal to that of the HPMC binder. The system also exhibits low torque and viscosity even at high shear rates. The extruded alumina obtained in this composition showed 65% green density and the same sample on sintering attained 98% density at 1500 °C. The sintered ceramic has an average grain size of 2–3 μm. The sol gel assisted colloidal processing yields extrudable alumina pastes with improved product quality. The study explored a process for alumina extrusion using boehmite gel as binder in addition to the effect of paste modifiers for alumina–boehmite systems.

References

[1] M.A. Janney, Plastic forming of ceramics: extrusion and injection moulding, in: R.A Terpstra, et al. (Eds.), Ceramics Processing, Chapman & Hall, UK, 1997, p. 174.

[2] P.M. Eggerstedt, J.F. Zievers, E.C. Zievers, Choose the right ceramic for filtering hot gases, Chem. Eng. Prog. 1 (1993) 62–68.

[3] H.T. Wang, X.Q. Liu, Y. Zhou, D.K. Peng, G.Y. Meng, Preparation and characterization of porous ceramic supports, Membr. Sci. Technol. 17 (1) (1997) 47–52.

[4] A.J. Fanelli, R.D. Silvers, W.S. Frei, J.V. Burlew, G.B. Marsh, New aqueous injection moulding process for ceramic powders, J. Am. Ceram. Soc. 72 (1989) 1833–1843.

[5] M.J. Cima, M. Dudziak, J.A. Lewis, Observation of poly(vinyl butyl)–dibutyl phthalate binder capillary migration, J. Am. Ceram. Soc. 72 (1989) 1087–1890.

[6] T. Zhang, S. Blackburn, J. Bridgwater, Properties of ceramic suspensions for injection moulding based on agar binder, Br. Ceram. Soc. Trans. 93 (6) (1994) 229–233.

[7] J.E. Scheutz, Methyl cellulose polymers as binders for extrusion of ceramics, J. Am. Ceram. Soc. 88 (1986) 1556–1559.
[8] Y. Chen, A. Burbidge, J. Bridgwater, Effect of carbohydrates on the rheological parameters of paste extrusion, J. Am. Ceram. Soc. 80 (7) (1997) 1841–1850.
[9] A.Y. Chen, J.D. Cawley, Extrusion of α-alumina–boehmite mixtures, J. Am. Ceram. Soc. 75 (3) (1992) 575–579.
[10] S. Amarasinghe, I. Wilson, On line monitoring of ceramic paste extrusion, J. Am. Ceram. Soc. 82 (9) (1999) 2305–2312.
[11] J.J. Benbow, E.W. Oxley, J. Bridgwater, The extrusion mechanisms of paste: the influence of paste formulation on extrusion parameter, Chem. Eng. Sci. 42 (1987) 2151–2162.
[12] B. Kindl, D.J. Carlsson, Y. Deslandes, A.J. Hoddenbagh, Preparation of α-alumina ceramics: the use of boehmite sol as dispersion agent, Ceram. Int. 17 (1991) 347–350.
[13] S. Ananthakumar, V. Raja, K.G.K. Warrier, Effect of nano particulate boehmite sol as dispersing medium for the slurry compaction of alumina ceramics, Mater. Lett. 43 (2000) 174–179.
[14] C. Sunilkumar, U.S. Hareesh, A.D. Damodaran, K.G.K. Warrier, Monohydroxy aluminium oxide as a reactive binder for extrusion of alumina ceramics, J. Eur. Ceram. Soc. 17 (1997) 1167–1172.
[15] S. Kwon, G.L. Messing, Constrained densification in boehmite–alumina mixtures for the fabrication of porous alumina ceramics, J. Mater. Sci. 33 (1998) 913–921.
[16] S. Ananthakumar, A.R.R. Menon, K. Prabhakaran, K.G.K. Warrier, Rheology and packing characteristics of alumina extrusion using boehmite gel as binders, Ceram. Int. 27 (2001) 231–237.
[17] J.S. Reed, Introduction to the Principles of Ceramics Processing, Wiley Publications, New York, 1988.
[18] J.J. Benbow, T.A. Lawson, E.W. Oxley, J. Bridgwater, Prediction of paste extrusion pressure, Am. Ceram. Soc. Bull. 68 (10) (1989) 1821–1824.
[19] S. Ananthakumar, K.G.K. Warrier, Gel assisted extrusion of alumina, Indian Ceram. Soc. Trans. 59 (2) (2000) 41–46.
[20] A.C. Pierre, D.R. Uhlmann, Gelation of aluminium hydroxide sols, J. Am. Ceram. Soc. 70 (1) (1987) 28–32.
[21] R.J. Huzzard, S. Blackburn, Influence of solids loading on aqueous injection moulding, Br. Ceram. Soc. Trans. 98 (2) (1999) 49–56.
[22] R. Moreno, The role of slip additives in tape casting technology. Part 1. Solvents and dispersants, Am. Ceram. Soc. Bull. 71 (10) (1992) 1521.
[23] R. Moreno, The role of slip additives in tape casting technology. Part 2. Binders and plasticizers, Am. Ceram. Soc. Bull. 71 (11) (1992) 1641.
[24] J. Zheng, J.S. Reed, S.K. Verma, Ceramic extrusion with PEG, Am. Ceram. Soc. Bull. 73 (12) (1994) 61–66.
[25] N.S. Sarkar Jr., G.K. Greminger, Methyl cellulose polymers as multifunctional processing aids in ceramics, Am. Ceram. Soc. Bull. 62 (11) (1983) 1280–1288.
[26] J.E. Schetz, Methyl cellulose polymers as binders for extrusion of ceramics, Am. Ceram. Soc. Bull. 65 (12) (1986) 1556–1559.
[27] B.V. Velamakanni, F.F. Lange, Effect of interparticle potentials and sedimentation on particle packing density of bimodal distribution during pressure filtration, J. Am. Ceram. Soc. 74 (1) (1994) 166–172.
[28] B.V. Velamakanni, J.C. Chang, F.F. Lange, D.S. Pearson, New method for efficient colloidal particle packing via modulation of repulsive lubricating hydrating forces, Langmuir 6 (1990) 1323.
[29] B.V. Velamakanni, F.F. Lange, F.W. Zok, D.S. Pearson, Influence of interparticle forces on the rheological behaviour of pressure consolidated alumina particle slurries, J. Am. Ceram. Soc. 77 (1) (1994) 216.
[30] C.S. Nordhal, G.L. Messing, Transformation and densification of nanocrystalline alumina during sinter forging, J. Am. Ceram. Soc. 79 (12) (1996) 3149–3154.