Journal of the European Ceramic Society **19** (1999) 2875–2881
© 1999 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0955-2219/99/$ - see front matter
PII: S0955-2219(99)00075-8

Gel Casting of Alumina Using Boehmite as a Binder

K. Prabhakaran,[a] S. Ananthakumar[b]* and C. Pavithran[a]

[a]Polymer Division, Regional Research Laboratory, Trivandrum, 695 019, India
[b]Structural Ceramics Unit, Regional Research Laboratory, Trivandrum, 695 019, India

(Received 11 December 1998; accepted 13 March 1999)

Abstract

The process for alumina gel casting was developed using an inorganic binder The monohydroxy aluminium oxide (boehmite, AlOOH) was incorporated with ultrafine alumina of particles (0·5 μm) and the slurry rheology was studied and presented. The effect of boehmite in slurry viscosity was observed with respect to different amounts of boehmite and time. The alumina 54 vol% slurry with 10 wt% boehmite showed the viscosity of 880 mPa s at 93 s^{-1}. An external coagulating agent, HMTA, was incorporated with alumina–boehmite slurry and the effective change in slurry viscosity with respect to concentration and time was studied. The addition of HMTA results in faster gelation and the optimum concentration was determined as 0·21 mol L^{-1}. The alumina gelcast body was dried under humidity conditions at 40°C, RH 70%. The defect free dried green body was obtained and the total linear drying shrinkage was calculated as 3·2% and the green density observed was 59·3% of theoretical value. The sintered density of 98% (TD) was achieved at 1450°C in 2 h. The mechanical hardness of sintered alumina measured as 2286 kg mm^{-2}. The sintered ceramic showed an extremely fine grained microstructure with an average grain size <2 μm. The boehmite acts as an excellent binder and sintering aid for alumina ceramics. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: Al_2O_3, gel casting, suspensions, microstructure-final, microstructure-prefiring.

1 Introduction

Fabrication of near-net-shape, ceramic parts requires high dimensional accuracy and more reliability. The existing forming methods like dry pressing, slip casting and injection molding have had limited success because of various problems associated with processing. In dry pressing, the fine ceramic powder is intentionally granulated for free flowing, and the variation of the bulk density of the powder granules during pressing results in non uniform powder packing.[1] Similarly, slip casting produces weak green bodies and further machining of engineering shapes becomes impossible.[2] The current injection molding technology possesses several shortcomings such as prolonged heating for binder burnout, molding defects, warpage and differential binder removal in thin and thick sections, that limit its use as a complex shape forming method.[3–5]

Gel casting is a well recognised and alternative route for fabricating strong, machinable green ceramic bodies.[6–9] The generic technique has been successfully applied to ceramics such as alumina, silicon nitride, sialon and Al_2O_3–SiC composites.[10,11] Recently, crystallographically textured iron titanate, a family of magnetically anisotropic ceramic was fabricated using gel casting.[12] A high strength porous alumina body was also fabricated by gel casting technique.[13] In general, the process consists of dispersing ceramic powder in a solution containing organic monomers, casting the suspension and initiating in-situ polymerization reaction to form a gelled body which will subsequently produce a solid green ceramic after drying. Conventional gel casting technology involves use of polymeric dispersants for obtaining free flow castable slurry with controlled rheology. However, it is observed that in polymer systems, though process of gelation and setting occurs in limited time, the removal of polymer from the green ceramic takes an extended period of heating time which will reduce the production rate. Use of inorganic binders overcomes such difficulties, and recently, boehmite has been identified as an inorganic binder

---

* To whom correspondence should be addressed.

for fabricating technical ceramics. Bruno Kindl used boehmite sol for dispersing alumina and found nanosize boehmite in alumina results in an early densification.[14] Chen and Cawley used boehmite gel as binder for alumina extrusion and produced high strength, highly dense alumina ceramic at 1450°C.[15] Also, seeded boehmite was used for the extrusion of ceria-zirconia ceramics and showed γ-alumina seeded boehmite results in uniformly distributed fine grained microstructure.[16] The main advantage identified was fast heating schedule for binder burnout without the formation of micro pores and cracks that are normally experienced in conventional methods. Similarly, boehmite, on heating, goes through various transitional alumina phases which can act as a sintering aid for alumina densification.

The present work is an attempt at gel casting of alumina ceramics using boehmite binder. The effect of boehmite as a binder and its influence in slurry viscosity at different shear rates, the change in viscosity with respect to time at constant shear rate, have been studied and presented. An external coagulating agent was incorporated, and the change in viscosity with respect to time and concentration of the gelling agent has been studied. The drying behaviour, linear drying shrinkage, green and sintered density have also been studied in addition to the mechanical strength and microstructural features.

2 Experimental Procedure

High purity alumina, A16 SG (ACC-Alcoa Chemicals, Calcutta, India) was used in this study. The powder has 99·9% purity, BET surface area 11 $\mathrm{m^2\,g^{-1}}$ and average particle size is 0·3–0·5 μm. The boehmite was procured from Condea Chemicals, Germany and has the particle density 3.1 $\mathrm{g\,cm^{-3}}$, BET surface area 177 $\mathrm{m^2\,g^{-1}}$ dispersibility and 25% loss on ignition. The crystallinity of alumina and boehmite was checked by X-ray diffraction. Hexamethylenetetramine, 99·9% purity (Fluka Chemicals, Switzerland) was used as gelling agent. The pH of the solution was controlled either by the addition of 0·1 N HNO_3 or 10% dilute NH_4OH. Double distilled water was used throughout the study. The as-received alumina powder was first rinsed and washed with dilute nitric acid to remove surface impurities, if any, and dried at 60°C for 48 h.

Alumina slurry consisting of 54 vol% solids was prepared and the viscosity was measured with and without boehmite. The concentration of boehmite was expressed as percentage by weight of alumina. The alumina slurry containing 5–15 wt% of bochmite was dispersed at pH 4 and was ball milled for 6 h to form uniform dispersion. A definite amount (10 ml) of slurry was poured into a cylindrical sample holder and the viscosity was measured by changing shear rates from 4·65 to 93 $\mathrm{s^{-1}}$ using S 21 spindle. The saturated solution of HMTA was added dropwise to the slurry under vigorous stirring and the viscosity change at different concentrations was measured. The time dependence of viscosity was also monitored. The yield stress of slurries was determined from viscosity data by graphical method.

2.1 Gel casting procedure

In a typical experiment 54 vol % of alumina slurry was prepared with 10 wt% of bochmite. The slurry was ultrasonicated for 30 min and pH was adjusted to 4. It was further ball milled for 6 h using alumina grinding media in polyethylene container to obtain highly dispersed unagglomerated ceramic slurry. The optimum quantity of HMTA was added drop wise under stirring conditions to obtain a flowable slurry. The whole mixture was continuously stirred for 15 min under vacuum before casting and poured into a cylindrical wax mould of 3 cm diameter and 5 cm height. The cast, after the gelation at room temperature was dried under humidity conditions at 40°C and 70% relative humidity (Humidity environmental chamber, REMI, India). The drying curve was drawn from the weight loss, observed at definite intervals. The humidity dried cast was removed from the mould and kept in an air circulated oven at 110°C for 12 h, before sintering. Green density and drying shrinkage of the cast was calculated from dimensional measurements. Thermomechanical analysis (TMA 50-11, Shimadzu, Japan) of the cast was carried out up to 1400°C at the rate of 10°C $\mathrm{min^{-1}}$ to study the sintering behaviour. Differential thermal analysis (DTA 50 H, Shimadzu, Japan) was also carried out to study the phase change characteristics of boehmite. The samples were sintered at 1450°C using programmable furnace (Nabortherm, Germany) as per the following sintering schedule.

$$\mathrm{RT} \xrightarrow{5^\circ\mathrm{C\,min^{-1}}} 500^\circ\mathrm{C} \xrightarrow{10^\circ\mathrm{C\,min^{-1}}} \underset{(60\text{ min soaking})}{900^\circ\mathrm{C}} \xrightarrow{15^\circ\mathrm{C\,min^{-1}}} \underset{(120\text{ min soaking})}{1450^\circ\mathrm{C}}$$

The furnace was allowed to cool by natural cooling. The sintered densities were determined by Archimedes' principle. The room temperature microhardness was measured by indendation method (Leitz' Micro hardness Tester, Germany). The fractured microstructure was observed using Scanning Electron Microscope (Hitachi, 2403 A, Japan).

3 Results and Discussion

Gel casting, in general, requires highly dispersed flowable suspension to form a high dense green ceramic. It has already been reported that the consolidation of powder suspension is driven by a chemical potential gradient in a given liquid phase and the factors governing particle packing are identified as solids loading and suspension rheology.[17] Previous reports have indicated that the total solids loading between 50 and 60 vol% is desirable for casting with controlled viscosity. In the present study, the effective solids loading to form a castable alumina suspension was 54 vol%, optimized from various trial experiments. The alumina 54 vol% slurry, at pH 4 forms highly dispersed, stable suspension of alumina particles and retains sufficient fluidity for casting. The cast obtained from alumina 54 vol% slurry shows the total theoretical green density of 62%. However, the strength of the cast is rather low and takes longer duration for setting which results in preferential settling of larger particles. In order to improve the green strength, boehmite was incorporated with alumina 54 vol% slurry and change in suspension rheology was studied.

3.1 Effect of boehmite

Figure 1 is the DTA pattern of alumina-boehmite mixture heated up to 1300°C at the heating rate of 10°C min^{-1}. The decomposition of boehmite occurs at various stages and the first endothermic peak at 101·59°C indicates the removal of physically adsorbed water from bochmite and the second endothermic peak at 453·88°C corresponds to the conversion of boehmite into γ-alumina. The final exothermic peak at 1178°C is attributed to the formation of more stable α-alumina. This is confirming that the boehmite becomes part of the parent matrix and can very well be used as binder for alumina ceramics.

The viscosity of the alumina 54 vol% slurry with and without boehmite at various concentrations was measured as a function of shear rate and presented in Fig. 2. In general the suspension shows 'shear thinning' flow behaviour. The alumina slurry without boehmite has very low viscosity that increases with the addition of boehmite. The addition of 5 wt% boehmite results in a viscosity of 400 mPa s at 93 s^{-1} that changes to 800 mPa s in 10 wt% boehmite containing suspension at the same shear rate. As the boehmite wt% is increased to 15, 54 vol% slurry forms a thick mass, making the viscosity measurements difficult. However on reducing the solids concentration of slurry to 47·5 vol%, viscosity was measured as 1020 mPa s at 93 s^{-1}. Since higher solids loading is essential, the 10 wt% of boehmite was fixed with 54 vol% slurry for casting. The yield stress value, calculated from viscosity data show the alumina 54 vol% slurry without boehmite is only 2·5 Pa and increases to 6·4 Pa for 5% boehmite. The 10% addition of boehmite gives the yield stress of 28·22 Pa. The increase of viscosity and yield stress of alumina suspension in presence of boehmite could be due to the particle size modifications to the lower size range.[18] Although the cast obtained from 54 vol% alumina–10 wt% bochmite slurry, has the workable green strength, the slurry takes a longer duration for setting and may result in mass segregation. Also, the cast during drying under humidity conditions produces surface cracks and pores due to the differential rate of drying and shrinkage.

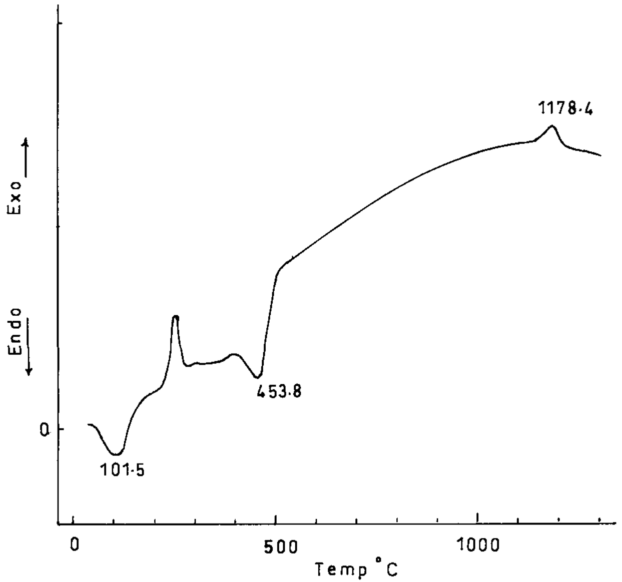

Fig. 1. DTA pattern of alumina–10 wt% boehmite mixture.

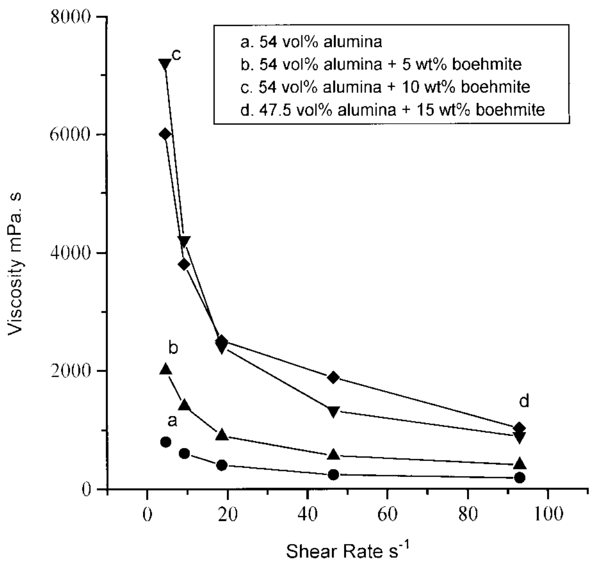

Fig. 2. Effect of shear rate on viscosity of alumina–boehmite slurry.

Figure 3 shows the viscosity change of alumina slurry with different boehmite content with respect to time. The viscosity, at constant shear rate, has no significant change even after 10 min of time, and the suspension maintains the fluid state. Gel casting process normally requires minimum setting time to avoid mass segregation, and high production rate. In order to achieve minimum setting time, an external coagulating agent was thought of and HMTA was selected. It was selected based on the following observations. HMTA was added separately with boehmite sol and alumina slurry at pH 4. The dispersed alumina in presence of HMTA did not show any gelation over a period of time or viscosity change. Whereas the boehmite sol at pH 4, in the presence of HMTA undergoes immediate gelation. This is possibly due to the bridging of bochmite particles by HMTA. The mechanism of bridging involves the exchange of proton between the hydroxyl group of boehmite and tertiary nitrogen of HMTA. The proposed mechanism is schematically shown in Fig. 4. An average effect was expected in alumina–boehmite mixture, in the presence of HMTA and the viscosity change with respect to time and concentration noted.

3.2 Effect of HMTA

Figure 5 shows the viscosity of 54 vol% alumina–10 wt% boehmite slurry with varying concentrations of HMTA. The viscosity value was measured at a constant shear rate of 18·65 s^{-1} after 1 min of shear. Addition of 0·21 mol L^{-1} HMTA caused an abrupt increase in viscosity from 2400 to 8400 mPa s. This increase is attributed to the rapid bridging of boehmite in presence of HMTA. The HMTA concentration below 0·126 mol L^{-1} did not show any appreciable change in viscosity. HMTA is protonated by H^+ ions in the suspension and hence the lone pair of the nitrogen atoms are not available for bridging and thus maintains low viscosity.

Figure 6 shows the viscosity change of alumina slurries containing 0·126 and 0·21 mol L^{-1} concentrations of HMTA at different shear rates. Generally, the shear thinning flow behaviour is observed. HMTA concentration at 0·126 mol L^{-1} has the viscosity of 1160 mPa s at 93 s^{-1} which is increased to 4800 mPa s at 4·65 s^{-1}. The viscosity rapidly changes with shear rate at higher HMTA concentrations and in the case of 0·21 mol L^{-1}, the viscosity of slurry changed from 1560 mPa s at 93 s^{-1} to 9600 mPa s at 4·65 s^{-1}. The high shear thinning behaviour at higher concentrations of HMTA is due to the breakdown of the bridges, formed between bochmite particles by proton exchange with HMTA. At concentrations >0·21

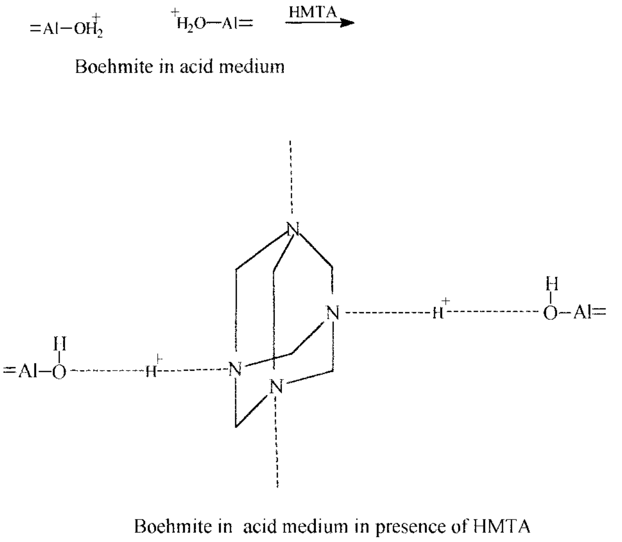

Fig. 4. Gelation mechanism of alumina–boehmite suspension in presence of HMTA.

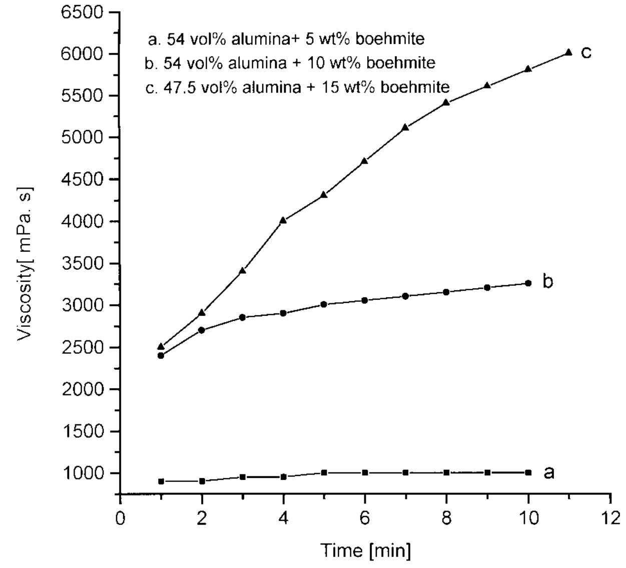

Fig. 3. Viscosity variation with time of alumina–boehmite slurry.

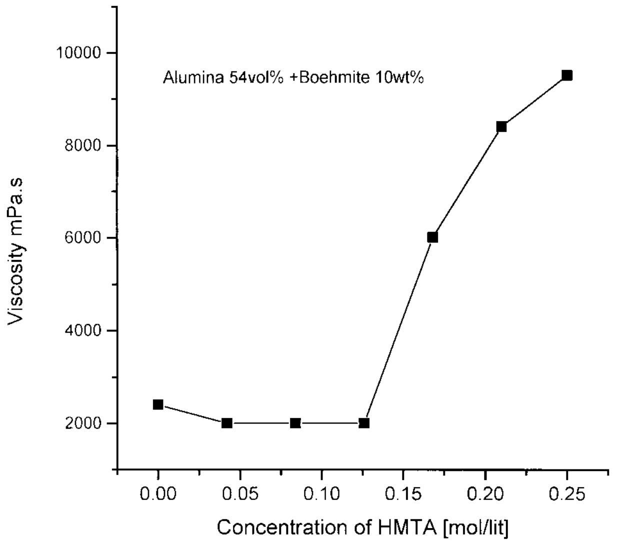

Fig. 5. Effect of HMTA on viscosity of alumina–boehmite slurry at different concentrations.

mol L^{-1}, the thickness of the suspension is too high leading to considerable decrease in flowability and hence is unsuitable for casting.

Figure 7 shows the time dependence of alumina suspension in presence of different concentrations of HMTA. The viscosity change was measured at 18·6 s^{-1}. The slurry viscosity increases rapidly in first few minutes and then gradually with time. This indicates that, the fast structural formation takes place due to rapid bridging. After 10 min of viscosity measurements, when the suspension was stirred vigorously with a glass rod, the suspension comes back to the original fluid state and follows the viscosity change with time similar to the one observed earlier. This indicates that there is a reversible nature of the bridging.

The composition of the mixture for suitable flow for casting under shear was optimized as 54 vol% alumina–10 wt% boehmite slurry to which 0·21 mol L^{-1} HMTA was added. The same slurry formed a soft gel with in 15 min after casting. In absence of any shear it remains as the gel, and when a high shear is induced the gel deforms to fluid state due to the collapse of bridging. This again confirms the reversible nature of bridging. During drying, the soft gel becomes a hard mass due to the in-situ coagulation of boehmite by ammonia released from the hydrolysis of HMTA. The reaction may be written as,

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6H - CHO + 4NH_3$$

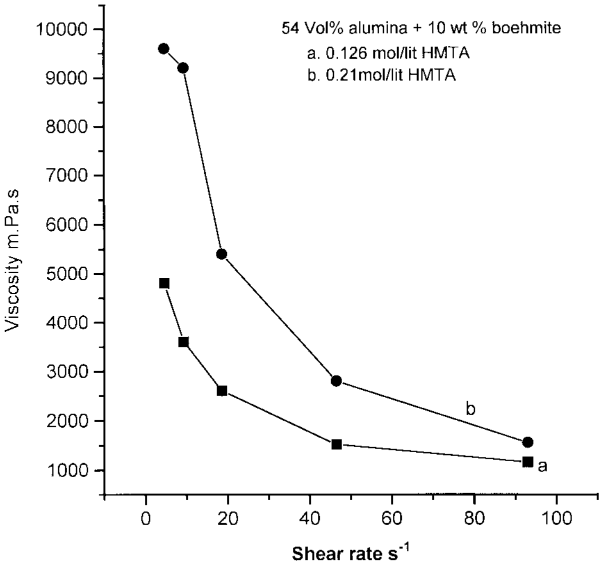

Fig. 6. Effect of shear rate on viscosity of alumina–boehmite slurry in presence of HMTA.

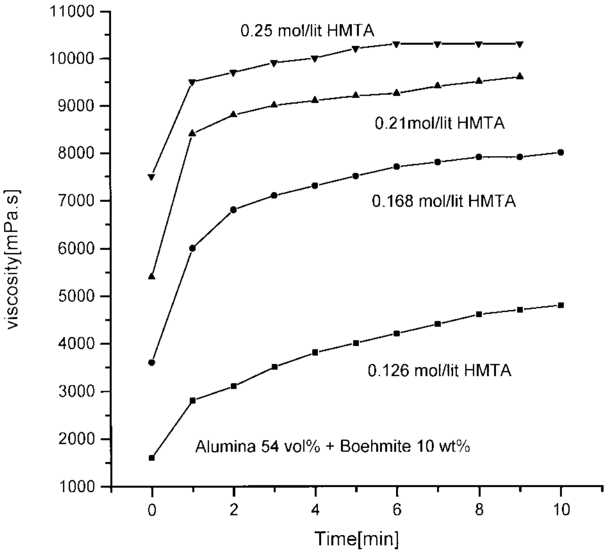

Fig. 7. Viscosity variation with time of alumina–boehmite slurry in presence of different concentrations of HMTA.

Figure 8 shows the drying behaviour of alumina–boehmite cast, under humidity conditions. Initially, the drying is very slow and water loss occurring upto 7 h of duration being 12%. Since the transport of water is possible only by capillary force, and it is a function of time and temperature, an extended time duration is required for drying. Moreover, the initial drying occurs mostly from the top surface layer. However, it was noted that the water loss increases gradually with drying time as

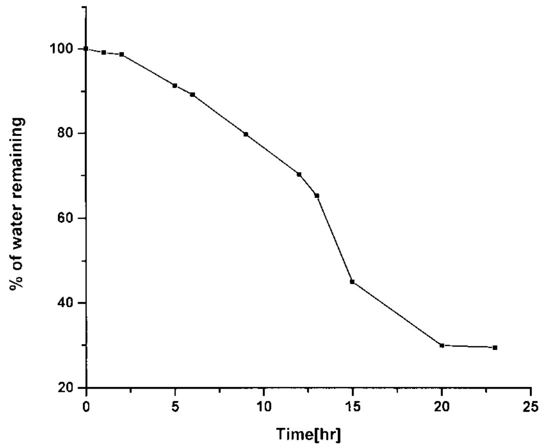

Fig. 8. Drying behaviour of alumina gelcast body under humidity conditions.

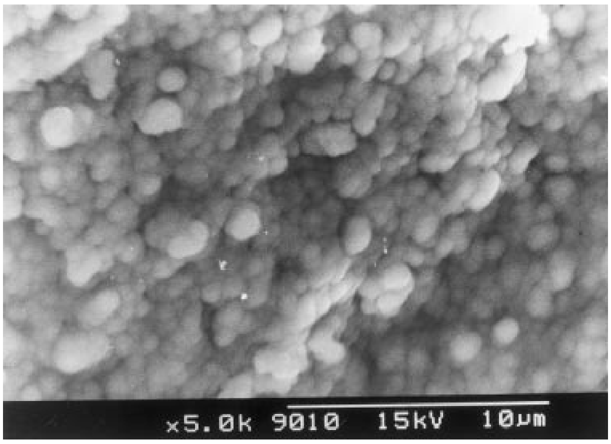

Fig. 9. SEM fractograph of alumina gelcast green body.

expected, the cast starts shrinking, uniformly after 7 h of time. Since the cast surface is exposed due to shrinkage, the drying occurs from all sides of the sample and results in faster drying. The linear shrinkage during drying is 3·2%, and volumetric shrinkage is 7·7%. This confirms that the technique can be used for producing near-net-shape ceramic bodies. The green density of the cast is calculated to be 59·30% of theoretical density. Figure 9 shows the SEM fractograph of green alumina gelcast sample in which close packing of alumina particles is observed. The green strength of the cast is fairly good as estimated qualitatively by abrasion test on coarse emery paper (Grit 360). This further indicates that the binding efficiency of the particle packing is high.

The TMA pattern of the alumina–boehmite cast in Fig. 10 showed the single step sintering behaviour, the densification starting at the much lower temperature of 1085°C. It indicates high sinterability of the cast. The closer particle packing and the presence of fine boehmite particles between the coarse alumina leads to sintering at lower temperatures and an early densification. It is already reported that the boehmite can act as sintering aid and the conversion of boehmite into γ-alumina during heat treatment also provides additional nucleating sites and facilitates densification of alumina.[19] The sintered density of the cast at 1450°C is found to be 3.87 g cm^{-3} (98% of theoretical value) and the Vicker's microhardness by indentation was 2286 kg mm^{-2} at 4.95 N. The total linear shrinkage after sintering is 15%. Figure 11 is the SEM fractograph of the sintered sample, and showed uniformly distributed, extremely fine microstructure ~2 μm grain size. Figure 12 shows the photograph of green and sintered alumina spur gear fabricated by this method.

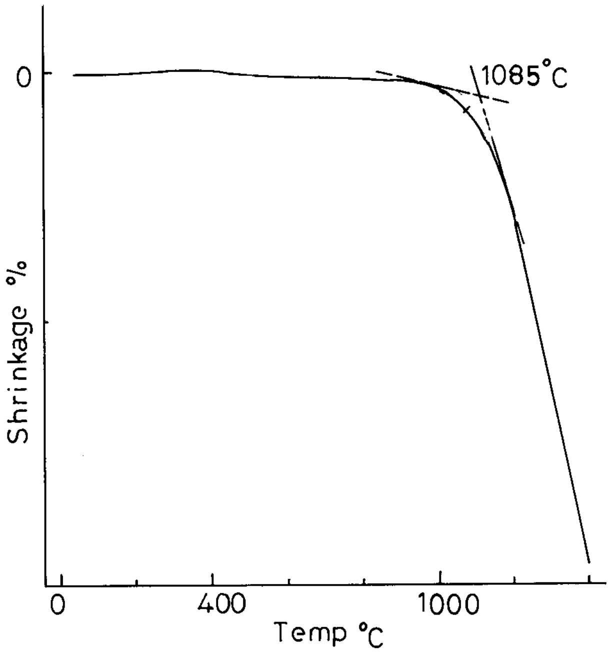

Fig. 10. TMA pattern of alumina gelcast body.

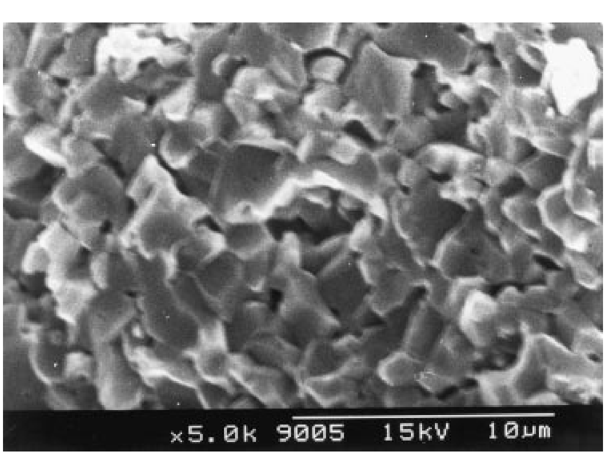

Fig. 11. SEM fractograph of sintered alumina gelcast body.

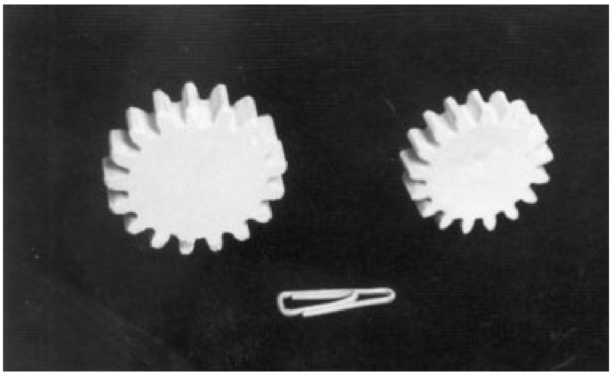

Fig. 12. Photograph of the green and sintered spur gear fabricated by this method.

4 Conclusions

A novel process for fabricating high density, near net shape alumina ceramic by gel casting using boehmite binder has been presented.

1. Addition of 10 wt% boehmite with 54 vol% alumina at pH 4, found to retain sufficient fluidity, suitable for casting.
2. The addition of 0.21 mol L^{-1} hexamethylenetetramine, acts as a coagulating agent and results in gelation within 15 min and preventing the preferential settling of larger particles, which is normally experienced in conventional methods. The gelation of alumina–boehmite slurry in the presence of HMTA is due to the exchange of proton between the OH group of boehmite and tertiary nitrogen of HMTA.
3. The alumina–boehmite slurry in the presence of HMTA showed the shear-induced flow behaviour and time dependence in viscosity.
4. The green body after drying has the total linear shrinkage of 3·2 and ~60% of theoretical green

density. The sintered density of 98% at 1450°C was achieved. The boehmite acts not only as binder but also provides additional nucleating sites and helps alumina sintering. The sintered ceramic has the hardness of about 2286 kg mm^{-2} and results in extremely fine grained microstructure.

References

1. Lange, F. F., Powder processing science and technology for reliability. *J. Am. Ceram. Soc*, 1989, **72**, 3–15.
2. St. Pierre, P. D. S., Slip casting of non clay ceramics. In *Ceramic Fabrication Processes*, ed. W. D. Kingery. MIT Press, Cambridge, MA, 1963, pp. 45–51.
3. German, R. M. and Hens, K. E., Key issues in powder injection moulding. *Am. Ceram. Soc. Bull*, 1991, **70**, 1294.
4. Edirisinghe, M. J. and Evans, J. R. G., Review: fabrication of engineering ceramics by injection moulding. 1. Materials selection. *Int. J. High. Tech. Ceramics*, 1986, **2**, 1–31.
5. Edirisinghe, M. J. and Evans, J. R. G., Review: fabrication of engineering ceramics by injection moulding. 11. Techniques. *Int. J. High. Tech. Ceramics*, 1986, **2**, 249–278.
6. Omatete, O. O., Janney, M. A. and Strelow, R. A., Gel casting—A new ceramic forming process. *Am. Ceram. Soc. Bull.*, 1991, **70**, 1641–1647.
7. Young, A. C., Omatete, O. O., Janney, M. A. and Menchofer, P. A., Gel casting of alumina. *J. Am. Ceram. Soc*, 1991, **74**, 612–618.
8. Takahashi, M. and Unuma, H., Gel casting. *Ceram. Jpn.*, 1997, **32**, 102–105.
9. Janney, M. A., Omatete, O. O., Walls, A., Nunn, S. D., Ogle, R. J. and Westmoreland, G., Development of low toxicity gel casting systems. *J. Am. Ceram. Soc*, 1998, **81**, 581–591.
10. Omatete, O. O., Strehiow, R. A. and Armstrong, B. L. Forming of silicon nitride by gel casting. In *Proceedings of the Annual Automotive Technology Development Contractors' Meeting*, Society of Automotive Engineers, Warrendale, PA, 1991, pp. 245–251.
11. Omatete, O. O., Strehlow, R. A. and Walls, C. A., Gel casting of submicron alumina. SIALON, and silicon nitride powders. In *Proceedings of the 37th Sagamore Army Materials Research Conference*, Plymouth, MA, 1990, pp. 201–212.
12. Zimmerman, M. H. and Faber, K. T., Forming texured microstructures via the gel casting technique. *J. Am. Ceram. Soc*, 1997, **80**, 2725–2729.
13. Pilar, S., Gelcasting foams for porous ceramics. *Am. Ceram. Soc. Bull.*, 1997, **76**, 61–65.
14. Kindl, B., Carlsson, D. L., Deslandes, Y. and Hoddenbagh, J. M. A., Preparation of alumina ceramics: the use of boehmite sol as dispersing agent. *Ceram. Int.*, 1991, **17**, 347–350.
15. Chen, A. Y. and Cawley, J. D., Extrusion of Al_2O_3 ceramics with low organic content. *Ceram. Eng. Sci. Proc*, 1989, **10**, 773–783.
16. Sunilkumar, C., Hareesh, U. S., Damodaran, A. D. and Warrier, K. G. K., Monohydroxy aluminium oxide (Boehmite, AlOOH) as a reactive binder for extrusion of alumina ceramics. *J. Eur. Ceram. Soc.*, 1997, **17**, 1167–1172.
17. Smith, P. A. and Haber, R. A., Effect of packing on the filtration and rheology behaviour of extended size distribution alumina suspensions. *J. Am. Ceram. Soc*, 1995, **78**, 1737–1744.
18. Smith, P. A. and Haber, R. A., Reformulation of an aqueous alumina slip based on modification of particle size distribution and particle packing. *J. Am. Ceram. Soc*, 1995, **75**, 1737–1744.
19. Tseng, T. Y., Kuo, Y. Y. and Lin, Y. L., Enhanced densification of pure alumina with alumina sol mixing. *J. Mat. Sci. Lett.*, 1989, **8**, 1274–1275.