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Gelcasting of alumina using the hexamethylenediamine–paraformaldehyde monomer system

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Abstract

A new aqueous alumina gelcasting system using hexamethylenediamine (HMDA) and paraformaldehyde monomers has been studied. The 500 vol% aqueous alumina slurries ‘A’ and ‘B’ containing paraformaldehyde and HMDA, respectively, undergo gelation after thorough mixing of the two due to the polymerization of HMDA and formaldehyde. The gelation time of the slurries cast in a mold is in the range of 7–2.4 min at HMDA to formaldehyde mole ratio in the range of 1.1–1.5. The faster reaction between HMDA and formaldehyde prevents the formaldehyde emission during the processing. The minimum HMDA to formaldehyde mole ratio required for the formation of a mechanically stable gel is 1.1. The compressive strengths and Young's modulus of the wet and dry alumina bodies increased with an increase in HMDA to formaldehyde mole ratio. Though the wet gelcast alumina bodies had low compressive strength (11.2–88.7 kPa) and Young's modulus (0.17–5.9 MPa) the dried ones showed high strength (6–11.7 MPa) and Young's modulus (209–364 MPa). The binder removal by slow heating to a temperature below 500 °C followed by sintering at 1600 °C produced alumina ceramics with ~97% of theoretical density.

Keywords: A. Shaping; C. Strength; D. Al_2O_3; Hexamethylenediamine; Paraformaldehyde

1. Introduction

Gelcasting is a well established method for the preparation of near-net-shape ceramic components [1–5]. In this, highly concentrated ceramic powder suspensions in an aqueous or non-aqueous medium are set in a mold by the *in situ* polymerization of organic monomers and cross-linking agents dissolved in the dispersion medium. The aqueous gelcasting system is preferred over the non-aqueous system due to the high cost and environmental pollution associated with the non-aqueous solvents. The free radical polymerization of many acrylic monomers and cross-linking agents has been studied for the gelcasting of various ceramic powder suspensions in aqueous medium [1–10]. The free radical polymerization of the acrylic monomers is inhibited by the atmospheric oxygen [11–13]. This results in the insufficient polymerization at the surface lead to the exfoliation of a layer from the surface of gelcast bodies. Therefore, the casting and setting of the ceramic powder suspensions need to be done in an inert atmosphere to avoid the interference of the atmospheric oxygen. The surface exfoliation of gelcast green bodies processed in air atmosphere could be prevented by adding water soluble polymers such as polyethylene glycol (PEG), poly acrylamide (PAM) and polyvinyl pyrolidone (PVP) into the gelcasting suspensions. However, the polymer addition increases the suspension viscosity [13–17]. Few non-acrylic organic monomer systems such as urea-formaldehyde and water soluble epoxy resins have been studied for the gelcasting of aqueous ceramic powder suspensions [18–22]. Gelation of aqueous powder suspensions by chemical cross-linking of water soluble polymers such as polyvinyl alcohol and chitosan using suitable cross-linking agents is also studied for gelcasting in air atmosphere [23–26]. Unlike the acrylic monomers, the addition of the epoxy resin and the water soluble polymers increases the suspension viscosity. On the other hand, the urea-formaldehyde system, though simple, did not get appreciation due to the irritating smell and toxic nature of the formaldehyde. The present work reports a new aqueous alumina gelcasting system using hexamethylenediamine (HMDA) and paraformaldehyde monomers. The use of paraformaldehyde (solid polymer of formaldehyde) instead of formaldehyde solution is expected to avoid the problem of formaldehyde emission during processing.

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2. Experimental

α-Alumina powder of average particle size 0.34 μm and specific surface area 10.4 m^2/g used was procured from ACC Alcoa, Kolkata. Analytical reagent grade HMDA and paraformaldehyde used were procured from Aldrich, USA and Merck India Ltd. Mumbai, respectively. The average particle size (measured using a particle size analyzer) of the paraformaldehyde powder was 2.8 μm. A 35 wt% aqueous ammonium poly (acrylate) solution (Darvan 821 A) used as dispersant was received from Vanderbilt company Inc., USA. The silicon free defoaming agent (BYK-023) used was obtained from BYK Chemie, Gmbh, Germany. Distilled water was used for the preparation of alumina powder suspensions.

The flow chart of the gelcasting process is shown in Fig. 1. Two 50 vol% slurries were prepared by dispersing 150 g alumina powder each in water using the ammonium poly (acrylate) dispersant. The ammonium poly(acrylate) used was 0.5 wt% of the alumina powder. The slurries were ball milled for 12 h in a roller ball mill using zirconia balls of 10 mm diameter. Alumina powder to zirconia ball weight ratio used was 1:4. The slurries were cooled in an ice bath to a temperature of nearly 5 °C. The calculated amount of paraformaldehyde was dispersed in one of the slurries by stirring with a glass rod and the HMDA was dissolved in the other slurry. The defoaming agent was added to both the slurries and the slurries were stirred well to achieve homogeneity. The slurries containing paraformaldehyde and HMDA are designated as A and B, respectively. The HMDA dissolved in slurry B was 4 wt% of the total alumina powder. The amount of paraformaldehyde dispersed in slurry A was equivalent to produce HMDA to formaldehyde mole ratio in the range of 1–1.5. The defoaming agent used was 0.05 wt% of the alumina powder. The slurry A was poured into the slurry B kept in an ice bath under constant stirring. The stirring was continued for another 2 min to achieve homogeneity. The gelcasting slurry thus obtained was cast in cylindrical polyvinyl chloride molds of 50 mm height and 25 mm diameter, respectively. The slurry cast in the mold was allowed to gel at room temperature. The gelled bodies removed from the mold were dried in the air atmosphere to a moisture content **of** less than 5 wt% and then in an air oven at 100 °C to form the green bodies. The green bodies were heated in a furnace at a rate of 1 °C/min up to 500 °C to remove the binder. The binder removed bodies were sintered at 1600 °C for 2 h in an electrically heated sintering furnace. The heating rate used was 5 °C/min.

The infrared (IR) spectrum of the HMDA-formaldehyde polymer was recorded in an IR spectrophotometer (Spectrum-150, PerkinElmer, USA) using an attenuated total reflectance accessory. The viscosity measurements of the alumina slurries were carried out using a Brookfield viscometer (Brookfield Engineering Inc., USA) with a small sample adapter and cylindrical spindle (SC-21). An approximate measurement of the gelation time was carried out as follows: the gelcasting

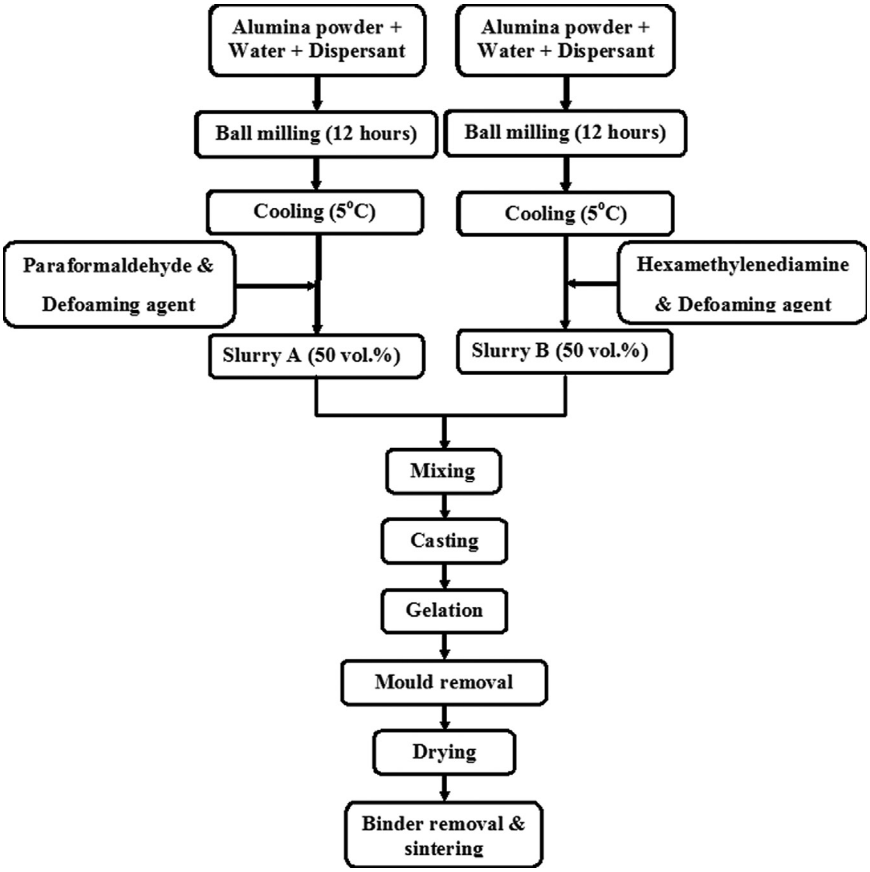

Fig. 1. Flowchart of the gelcasting process.

slurry was continuously stirred with a glass rod and the time at which the slurry loses its flow was taken as gelation time. The linear shrinkages during the drying and sintering were measured from the initial and final dimensions of the bodies. The green and sintered densities were calculated from the weights and dimensions of the green and sintered alumina bodies, respectively. The microstructures of the green and sintered alumina bodies were observed on the fractured surfaces using a scanning electron microscope (SEM, Zeiss EVO 18, Special Edition, USA). The thermogravimetric analysis of the green alumina sample was carried out in the air atmosphere at a heating rate of 10 °C/min using a thermal analyzer (Q-50, TA Instruments, USA). The compressive strength of the gels and green bodies was measured using a Universal Testing Machine (Instron 4469, UK) at a cross head speed of 2 mm/min.

3. Results and discussion

The HMDA reacts with formaldehyde solution to form a polymer [27]. The reaction is instantaneous even in the ice cold conditions. Therefore, gelcasting using this polymerization reaction is difficult as we will not get sufficient time for mixing and casting the slurries. It is well known that paraformaldehyde, the polymeric form of formaldehyde, sparingly dissolves in cold water and slowly releases formaldehyde. Therefore, a considerable increase in gelation time is expected when the paraformaldehyde is used in place of formaldehyde. However, lumps were formed when an ice cold alumina slurry containing HMDA is mixed with the paraformaldehyde powder due to the inhomogeneous gelation by localized polymerization before proper dispersion of the paraformaldehyde. This makes the uniform mixing of paraformaldehyde with the slurry difficult. Moreover, the slurry undergoes complete gelation in 5–10 min at HMDA to formaldehyde mole ratio in the range of 1.1–1.5. It appears that the paraformaldehyde–formaldehyde equilibrium shifted to the right as the formaldehyde generated is instantaneously consumed by the HMDA. This observed gelation time is not sufficient for the proper wetting and mixing of the paraformaldehyde with the slurry. The inhomogeneous gelation and insufficient time for mixing and casting, limited the possibility of a one pack system for gelcasting using the HMDA–paraformaldehyde monomers.

In order to increase the automation to aid the industrialization of gelcasting process, a two pack slurry system was used [1,28–31]. In this, two slurries, A and B, of the ceramic powder are prepared in which the monomer, cross-linker and catalyst are added with the slurry A and the initiator is added with the slurry B. The two slurries were thoroughly mixed before casting into the mold. Mixing of the two slurries brings the monomer, initiator and catalyst together resulted in a polymerization reaction leading to the gelation [28]. A similar approach would overcome the problem of insufficient mixing and casting time in the HMDA–paraformaldehyde system. In the present case, the alumina slurry A containing paraformaldehyde is poured into the slurry B containing HMDA with vigorous stirring using a glass rod. The mixing time was 2 min irrespective of the HMDA to formaldehyde mole ratio. Addition of the defoaming agent in both the slurries prevents the formation of stable bubbles during the mixing, which avoids the necessity of degassing before casting.

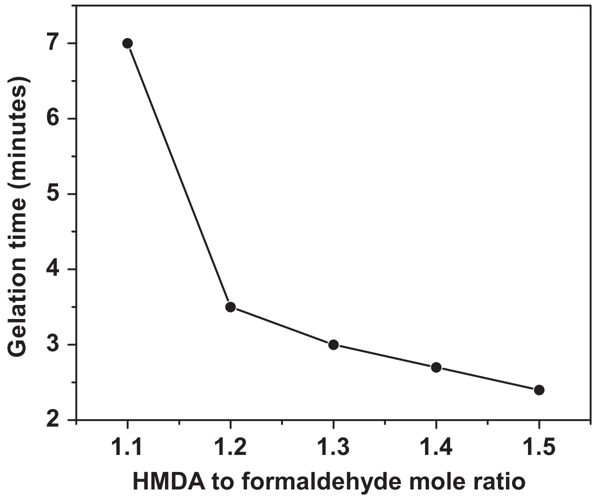

Fig. 2. Effect of HMDA to formaldehyde mole ratio on the gelation time of gelcasting slurries.

The gelcasting slurries cast in a mold undergo gelation within a short time. The gelation time decreased from 7 to 2.4 min when the HMDA to formaldehyde mole ratio increased from 1.1 to 1.5. Fig. 2 shows the gelation time of the gelcasting slurries at various HMDA to formaldehyde mole ratios. The lower gelation time at higher HMDA to formaldehyde mole ratio is due to the faster polymerization and cross linking at higher formaldehyde concentrations. Though the gelcasting slurries prepared at the HMDA to formaldehyde ratios in the range of 1.1 to 1.5 had very good fluidity for casting, the viscosity measurement at HMDA to formaldehyde mole ratio above 1.1 is difficult, as the time required for the viscosity measurement is higher than the gelation time. However, at HMDA to formaldehyde mole ratio 1.1, the slurry viscosity remains unchanged for sufficient time for the successful measurement of viscosity. Fig. 3 shows the viscosity at various shear rates of the slurry A, slurry B and the gelcasting slurry obtained by mixing the two at a HMDA to formaldehyde mole ratio 1.1. The slurries showed shear thinning flow behavior. The slurry A, slurry B, and the gelcasting slurry showed more or less the same viscosity. The viscosity of the gelcasting slurry is in the range of 0.4 to 0.2 Pa s at shear rates in the range of 4.65 to 93 s^{-1}.

The IR spectrum of the polymer prepared at HMDA to formaldehyde mole ratio of 1.5 is shown in Fig. 4. The peaks at 3366 and 1640 cm^{-1} are attributed to the N–H stretching and bending vibrations, respectively, of secondary amine. The IR peaks at 2928, 2854 and 1467 cm^{-1} are due to the stretching and bending vibrations of C–H bond. The peaks appeared at 1365 and 1127 cm^{-1} are corresponding to the stretching vibrations of amine C–N and ether C–O, respectively. The peak at 724 cm^{-1} is due to the $–CH_2–$ groups from HMDA. The chemical reactions leading to the gelation of the slurry is shown in Fig. 5. The formaldehyde generated from the paraformaldehyde reacts with HMDA to form methylol

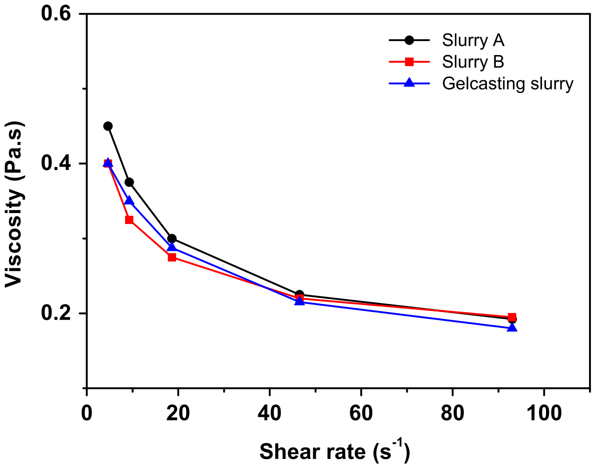

Fig. 3. Viscosity at various shear rate of the gelcasting slurry.

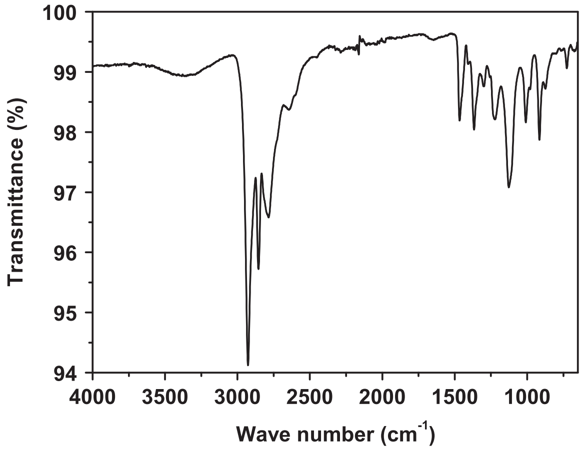

Fig. 4. Infrared spectrum of HMDA–formaldehyde polymer.

derivatives. The methylol derivatives further react with HMDA and formaldehyde to form the low molecular weight HMDA–formaldehyde polymer molecules. The low molecular weight polymer molecules undergo further cross-linking through C–O–C linkages. The strength of the wet gelcast bodies depends on the extent of cross-linking and the extent of cross-linking depends on the HMDA to formaldehyde mole ratio. The gelcast wet bodies prepared at HMDA to formaldehyde mole ratio of 1 did not have sufficient strength to withstand its weight. On the other hand, the wet bodies at HMDA to formaldehyde mole ratio of 1.1 and above could be easily removed from the mold without any deformation. Fig. 6 shows the photograph of the gelcast bodies at HMDA to formaldehyde mole ratios of 1 and 1.1 immediately after the mold removal. We did not feel the smell of formaldehyde during the mixing and casting as the formaldehyde produced from the paraformaldehyde is instantaneously consumed by the HMDA for the polymerization.

The stress–strain graph of the gelcast wet bodies prepared at various HMDA to formaldehyde mole ratios is shown in Fig. 7. Except at the HMDA to formaldehyde ratio of 1.1, the stress–strain graph showed an elastic region followed by a yield point and a stress maximum. Cracks were formed on the test samples at the point of stress maximum followed by a decrease of stress. At the HMDA to formaldehyde mole ratio of 1.1, the sagging of the sample was observed with a plateau region in the stress–strain graph after reaching the stress maximum. The stress maximum observed in the stress–strain graph is taken as the compressive strength. The percentage strain at which the stress maximum observed decreases with an increase in HMDA to formaldehyde mole ratio. Fig. 8 shows the effect of HMDA to formaldehyde mole ratio on the compressive strength and Young's modulus of the gelcast wet alumina bodies. The compressive strength and Young's modulus increased from 11.2 to 188.7 kPa and 0.17 to 5.9 MPa, respectively, when the HMDA to formaldehyde mole ratio increased from 1.1 to 1.5. The increase in compressive strength and Young's modulus with an increase in HMDA to formaldehyde mole ratio is due to the increase in number of cross-links in the HMDA–formaldehyde polymer. The values obtained are in the range of compressive strength and Young's modulus reported for wet alumina bodies prepared by direct coagulation casting [32,33]. On the other hand, strength and modulus reported for the gelcast wet bodies prepared by acrylic and epoxy monomers were higher than these values. It appears that the fast reaction between HMDA and formaldehyde leads to a polymer with low molecular weight that resulted in the relatively low compressive strength and Young's modulus of the gelcast wet alumina bodies.

The gelcast bodies removed from the mold took nearly five days to reach a moisture content of less than 5 wt% on drying in air atmosphere at room temperature. No cracks or deformations were observed on the bodies during the drying. The linear drying shrinkage decreased from 5.5% to 4.6% when the HMDA to formaldehyde mole ratio increased from 1.1 to 1.5. On the other hand, the density of green bodies obtained was in a close range of 56.47% to 56.84% of theoretical density. The compressive strength and Young's modulus of the gelcast alumina green bodies increased from 6 to 11.7 MPa and 209 to 364 MPa, respectively, when the HMDA to formaldehyde mole ratio increased from 1.1 to 1.5. Fig. 9 shows the compressive strength and Young's modulus of the gelcast alumina green bodies at various HMDA to formaldehyde mole ratios. The relatively high compressive strength of the green bodies indicates that the molecular weight of HMDA-formaldehyde polymer increased due to cross-linking through the intermolecular –OH condensation during the drying. The increase in compressive strength and Young's modulus with an increase in HMDA to formaldehyde ratio is due the increase in the number of cross-links.

Fig. 10 is the TGA showing the thermal decomposition of HMDA–formaldehyde polymer in the gelcast alumina sample. The weight loss pattern of the gelcast sample and the neat polymer is more or less the same. However, the decomposition of the polymer in the gelcast sample takes place at lower temperatures compared to that of the neat polymer. The complete polymer burnout from the gelcast sample takes place at 500 °C whereas the decomposition of the neat polymer is extended up to 620 °C. This indicates that the alumina powder catalyzes the thermal decomposition of the HMDA–formaldehyde polymer.

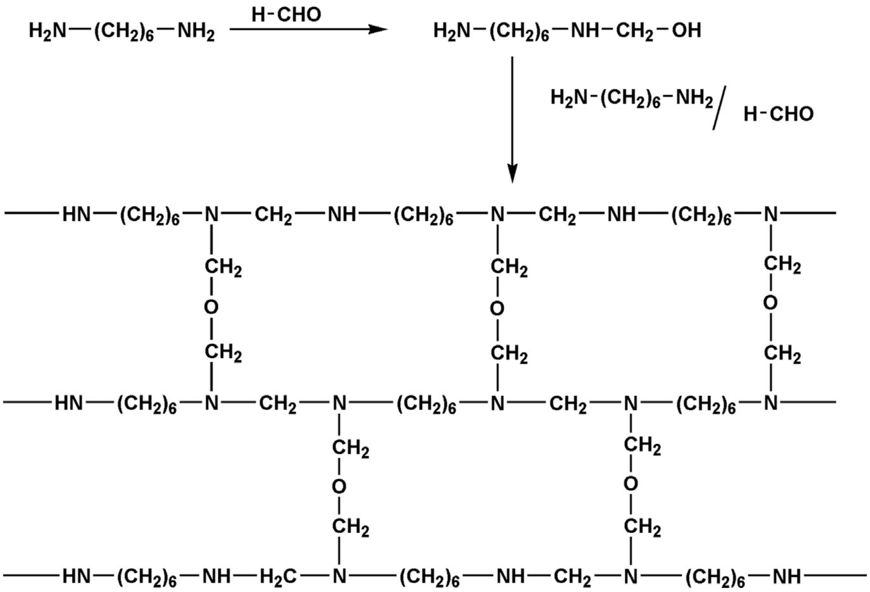

Fig. 5. Chemistry of the gelation process.

Fig. 6. Photograph of gelcast wet alumina bodies prepared at HMDA to formaldehyde mole ratio of 1 (left) and 1.1 immediately after mold removal.

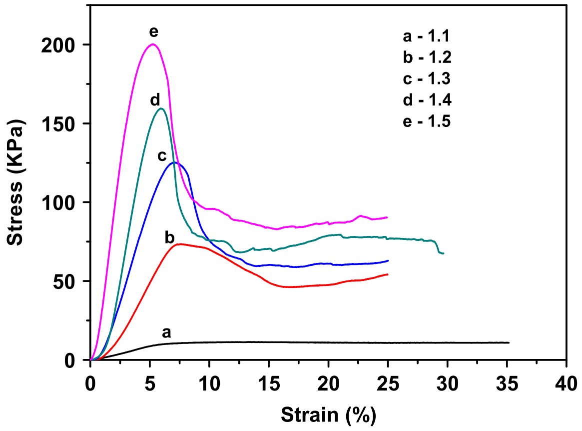

Fig. 7. Stress–strain curve of gelcast wet bodies prepared at various HMDA to formaldehyde mole ratios.

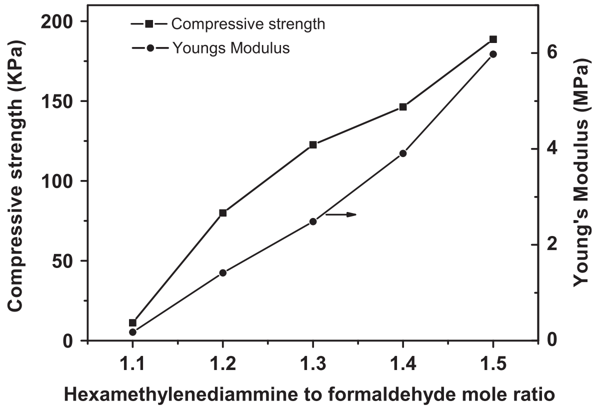

Fig. 8. Effect of HMDA to formaldehyde mole ratio on the compressive strength and Young's modulus of gelcast wet alumina bodies.

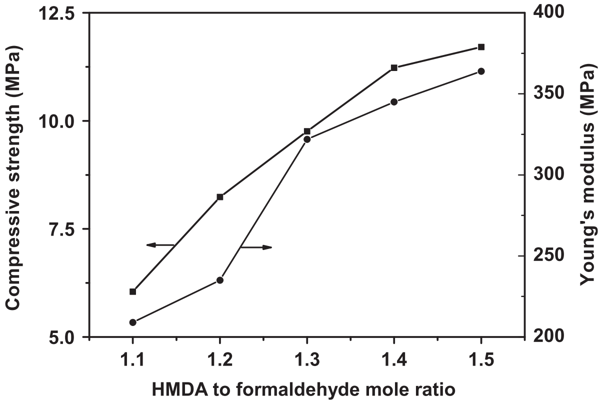

Fig. 9. Effect of HMDA to formaldehyde mole ratio on the compressive strength and Young's modulus of gelcast green alumina bodies.

The cylindrical samples of 50 mm length and 25 mm diameter did not show any crack during polymer burnout by heating in a muffle furnace at a rate of 1 °C/min. We have suspected the

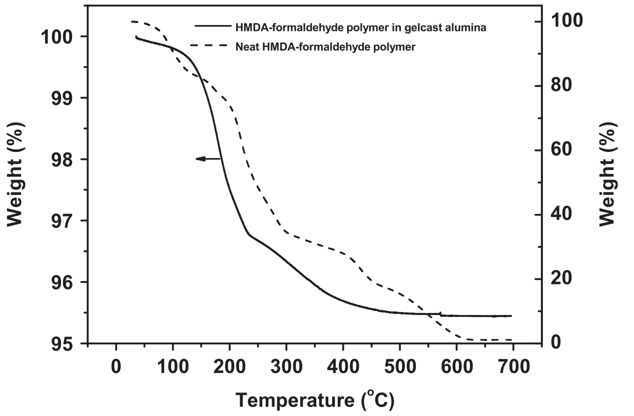

Fig. 10. TGA of the gelcast alumina sample (HMDA to formaldehyde mole ratio 1.5).

presence of unreacted paraformaldehyde particles and their agglomerates in the gelled alumina bodies. Fig. 11 shows the SEM photomicrograph of the fractured surface of the alumina green body after the polymer burnout. There are no macro pores observed in the microstructure, indicating the complete dissolution of the paraformaldehyde particles to form HMDA–formaldehyde polymer.

The gelcast bodies achieved 96–97.4% of theoretical density during sintering. The linear sintering shrinkages observed were in the range of 16.4–16.9% at HMDA to formaldehyde mole ratio in the range of 1.1–1.5. Fig. 12 shows the SEM photomicrograph of fractured surface of a sintered gelcast alumina ceramic. The microstructure shows inter granular fracture. No macro pores were observed in the microstructure of the sintered alumina ceramic. The process enables the fabrication of near-net-shapes. Fig. 13 shows the photograph of a near-net-alumina shape fabricated by the new gelcasting system.

4. Summary

Gelcasting of aqueous alumina slurries was carried out using HMDA and paraformaldehyde monomer system. The paraformaldehyde powder dispersed in the alumina slurry ‘A” reacts with the HMDA dissolved in the suspension medium of the alumina slurry ‘B” to form a gel when the two slurries were thoroughly mixed and cast in a mold. The gelation time decreased from 7 to 2.4 min when the HMDA to formaldehyde mole ratio increased from 1.1 to 1.5. The minimum HMDA to formaldehyde mole ratio required for the formation of a mechanically stable gel from the 50 vol% alumina slurries is 1.1. The compressive strength of wet and dry gelcast alumina bodies increased with an increase in HMDA to formaldehyde mole ratio due to the increase in number of cross-links. The wet gelcast alumina bodies showed relatively low compressive strength (11.2–88.7 kPa) and Young's modulus (0.17–5.9 MPa) due to the low molecular weight of HMDA–formaldehyde polymer. The green alumina bodies showed high compressive strength (6–11.7 MPa) and Young's modulus (209–364 MPa) due to further cross-linking during the drying. The complete polymer burnout from gelcast alumina green bodies could be

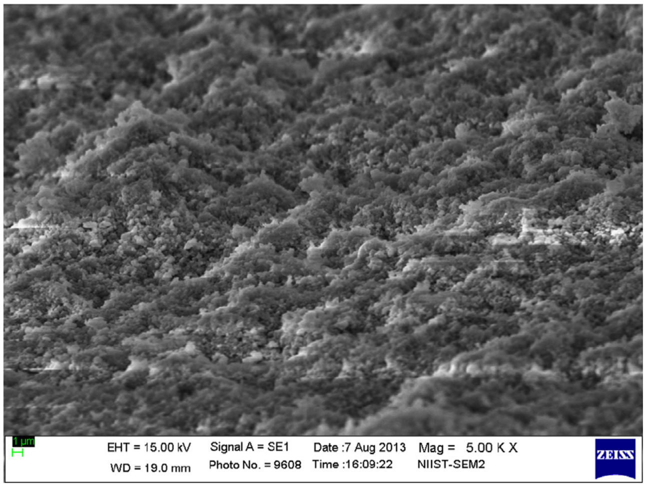

Fig. 11. SEM photomicrograph of the green alumina body after binder removal.

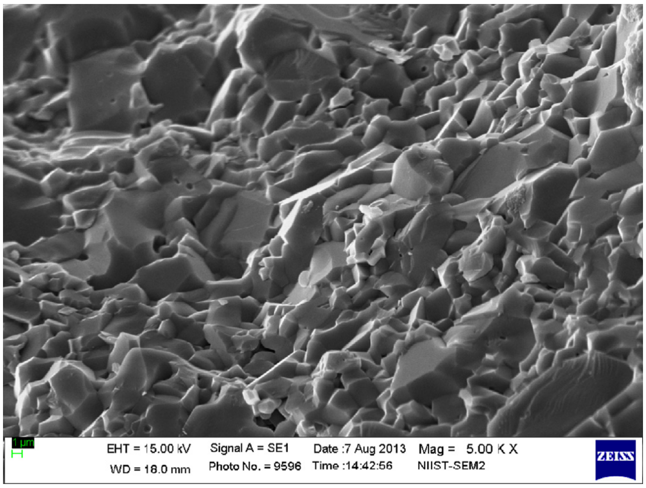

Fig. 12. SEM photomicrograph of fractured surface of sintered alumina ceramic prepared by the gelcasting process.

Fig. 13. Photograph of a near-net-alumina shape fabricated by the gelcasting process.

possible by heating at a temperature of less than 500 °C. The gelcast bodies achieved 96–97.4% of theoretical density during sintering.

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