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Preparation of macroporous alumina ceramics using wheat particles as gelling and pore forming agent

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Abstract

The present work reports a simple process for preparation of macroporous alumina ceramics from aqueous powder slurries using wheat particles as gelling and pore forming agent. Wheat particles incorporated in aqueous alumina slurries rapidly absorb water on heating and transform it into a strong gel. The gelled bodies did not undergo crack and warpage during drying. The dried green bodies showed diametrical compressive strength in the range 0.41–0.59 MPa and are amenable to machining operations such as milling, drilling and lathing. Pyrolytic removal of the pore former followed by sintering at 1600 °C produced alumina bodies with porosity 67–76.7% and diametrical compressive strength 2.01–5.9 MPa. Isotropic shrinkage was observed during sintering. Microstructure showed both large (200–800 μm) and small (less than 20 μm) pores. Small pores were uniformly distributed in the struts and walls of the large pores.

Keywords: A. Processing; B. Porosity; Alumina; Gelation

1. Introduction

Porous ceramics are widely used in applications such as thermal insulation, filter media, fuel cell electrodes, catalyst support, impact absorbing structures and preform for ceramic–metal and ceramic–polymer composites [1–3]. They are prepared mainly from colloidal suspensions of the respective ceramic powders. Processes like polymer foam impregnation, gel casting, freeze drying and tape casting have been used for the consolidation of the powder suspensions into porous bodies. In polymer foam impregnation process, ceramic replica of a polymer foam is prepared by soaking polyurethane foam of desired pore size in a ceramic powder suspension followed by squeezing the excess slurry out by rolling, drying the slurry impregnated polymer foam, careful burnout of organics and sintering [3–7]. In gel casting, a ceramic powder suspension containing organic monomer and cross linking agent is foamed by using a blowing agent followed by setting by in situ polymerization of the monomer [8–10]. The method produces green ceramic foams with machinable strength. Gel casting produces porous ceramics with a combination of open and closed pore microstructure having superior mechanical properties in wide range of porosities. However, the process has limitations with respect to the control of pore size. In freeze drying process, controlled crystallization of ice is used for consolidation of aqueous powder suspensions into bodies and sublimation of the ice crystals under reduced pressure resulted in porous structure [11]. In tape casting process, ceramic powder suspension containing pore formers such as carbon particles and polymer beads is made into thin layers using a blade. Burnout of these pore formers followed by sintering produces porous ceramics with porosity up to 70% [12–14]. The method is suitable for preparation of layered composites containing porous layers [15,16]. Preparation of three dimensionally ordered macroporous ceramic structures has been recently reported using polymer beads as template for macro-pores [17–21]. In this case, polymer beads are either incorporated to the system during sol–gel processing or coated with ceramic slurry and then consolidated. Burnout of the polymer beads from the consolidated bodies creates three dimensionally ordered macro pores. Thijs et al. [22] used a seed and a pea as template for macro pores in a two step slurry coating process route for producing ceramic foams.

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Recently, proteins such as ovalbumine (freshly extracted egg white) and bovine serum albumin have been used for the foaming and setting of aqueous ceramic powder suspensions for preparation of porous ceramics [23–25]. In this, thermal-induced coagulation of the proteins is used for setting of foamed suspensions. Lyckfeldt and Ferreira [26] reported a starch consolidation process for preparation of porous ceramics. In this process, native and chemically modified potato starch granules were incorporated into aqueous ceramic powder suspensions and the slurry was further consolidated into near-net-shape bodies by heating in the temperature range 60–80 °C. Characteristics such as higher water absorption and swelling of starch in this temperature range is used for the gelation of the slurry. The process produces porous ceramics with 30–70% porosities. The pore size depends on the size of starch granules which is nearly 50 μm. Wheat is a low cost starchy material which can be powdered into particles of any size. The present work explores the possibility of using wheat particles as gelling agent and pore forming agent for preparation of porous alumina ceramics.

2. Experimental

Alumina powder (A16SG, ACC Alcoa, India) of average particle size 0.34 μm and surface area 10.4 m^2/g was used. Distilled water was used for preparation of slurries. Nitric acid (Merck, India) was used for pH adjustments. Wheat particles used were food grade and procured from local market. Ash content of the wheat particles was 0.33 wt.% (estimated gravimetrically by heating at 1000 °C for 2 h in a platinum crucible).

Forty-five vol% slurry was prepared by dispersing the alumina powder in water and adjusting the pH to 3.5 using dilute nitric acid. The slurry was ball milled for 6 h in a polyethylene container using zirconia balls. The slurry was diluted with required amount of water to prepare powder suspensions of various solids contents. Wheat particles were added to the alumina powder suspensions with constant stirring. The amount of wheat particles added was restricted to a level to keep the slurry flowable for casting. The studied compositions are given in Table 1. Viscosity of the slurries was measured in a Haake-RV3 (Thermo Electron Corp, Germany) viscometer using cylindrical spindle (MV3). Apparent yield stress values of the slurries were calculated from viscosity data by graphical method [27]. The slurry was cast in cylindrical/rectangular open stainless steel mould and heated in an air oven at 100 °C for 30 min. Castor oil was used as lubricant for easy mould removal. The gelled body removed from the mould was dried in oven at 80 °C for 24 h and then at 120 °C for 8 h. TGA (Hi Res TGA 2950, TA Instruments, USA) analysis of the wheat powder particles and green alumina samples were carried out in air atmosphere at a heating rate of 10 °C/min. The dried samples were heated in a furnace at a rate of 0.5 °C/min up to 350 °C and 2 °C/min up to 600 °C for removal of the wheat particles and then at a rate of 5 °C/min up to 1600 °C. A holding time of 2 h was given at 1600 °C. Density of the sintered samples was determined from dimensional measurement. Microstructure of sintered samples was observed in a scanning electron microscope (LEO 1455, UK).

Table 1
Slurry compositions

Composition	Alumina (gm)	Water (ml)	Wheat particles (gm)	Yield stress of slurry (Pa)
A	100	75	50	112
B	100	100	71	132
C	100	125	81	137
D	100	150	96	159

Mechanical strength of the green and sintered samples was measured in a universal testing machine (Hounsfield, S-sires, UK) by diametrical compression at a loading rate of 5 mm/min. Green samples of 30 mm diameter and 10 mm length and sintered samples of 25 mm diameter and 8.3 mm length were used for diametrical compression testing. Strength was calculated from the breaking load using the equation $S = 2P/\Pi LD$, where S, P, L and D are diametrical compressive strength, breaking load, sample length and sample diameter, respectively [28]. Machinability of green bodies was checked by making holes by drilling and slots by grinding in lathing machine using conventional tools.

3. Results and discussion

Fig. 1 shows SEM microstructure of the wheat particles. Most of the particles have sizes in the range 200–800 mμ and irregular shape. Wheat particles when mixed with water slowly absorb water at room temperature. The particles in wheat particle–water mixture at room temperature are found non-sticky. However, on heating, particles absorb water rapidly and transform the mixture into a strong gel. It has been observed that 35 gm of the wheat particles absorb 100 ml water at 100 °C and form a strong gel. When stirred with alumina powder suspension the wheat particles disperse well without any agglomeration. After incorporation of optimum amount of wheat particles the slurries had near to a paste consistency. The viscosity of the slurries measured at various shear rates is shown in Fig. 2. All the viscosity measurements were carried

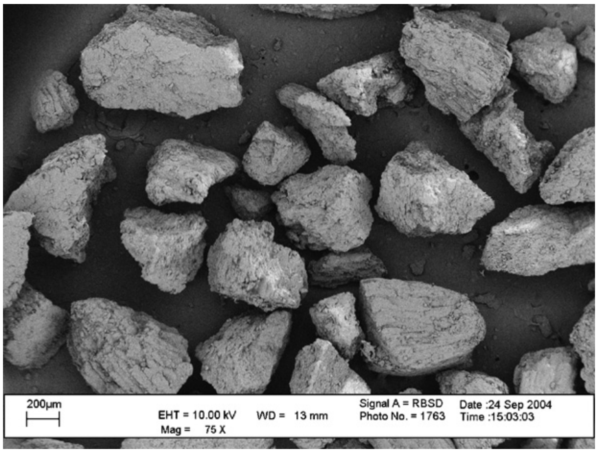

Fig. 1. SEM photograph of wheat particles.

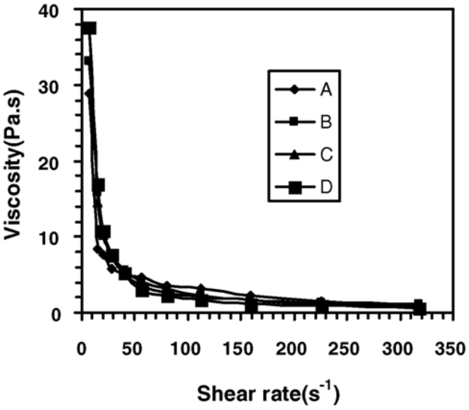

Fig. 2. Viscosity versus shear rate of alumina slurries containing wheat particles (compositions A–D).

out within 10 min after mixing. The slurries showed pseudoplastic flow behaviour. Though the slurries (A–D) showed large difference in viscosity (28.8–37.5 Pa s) at low shear rate (7 s^{-1}) the viscosity values are very close at high shear rate. The viscosity value of the slurries at high shear rate (318.5 s^{-1}) is in the range 0.6–1.1 Pa s indicating that the slurries are pourable under shear. The apparent yield stress values determined from viscosity data was 112, 132, 137 and 159 Pa for slurry compositions A, B, C and D, respectively. Relatively high yield stress values confirms near to paste consistency of the slurry which prevented gravitational sedimentation of the wheat particles. Thus, casting was performed under shear and vibration was applied after casting for proper mould filling. The slurries cast in cylindrical/rectangular mould when heated in an air oven at 100 °C for 30 min undergo gelation. The gelled bodies have sufficient strength for removal from the mould and for further handling. It is worthy to note that in all slurry compositions tested, wheat particles to water weight ratio is greater than 0.35, which enabled formation of strong gel.

The gelled bodies undergo shrinkage in the range 5.6–20.1 vol% on drying at 80 °C in an air oven. The drying shrinkage values for gelled bodies prepared from various slurry compositions is given in Table 2. The composition D showed remarkably high shrinkage and slight warpage during drying. Therefore, further increase in wheat particle concentration was not attempted. The diametrical compressive strength of green bodies prepared from slurries of various compositions is given in Table 2. The strength decreases with increasing wheat particles concentration in the body. The compositions tested showed diametrical compressive strength in the range 0.59–0.41 MPa, which is comparable to dry pressed green alumina samples using PVA binder [22]. The green bodies showed good machinability characteristics. They are amenable to drilling, grinding and lathing using conventional tools.

Table 2
Characteristics of green and sintered alumina samples

Composition	Drying shrinkage (vol%)	Green strength (MPa)	Sintering shrinkage (vol%)	Porosity (%)	Strength (MPa)
A	5.6	0.59	42.6	67.0	5.9
B	6.2	0.51	45.0	72.2	3.1
C	13.6	0.50	46.6	75.1	2.3
D	20.1	0.41	47.7	76.7	2.0

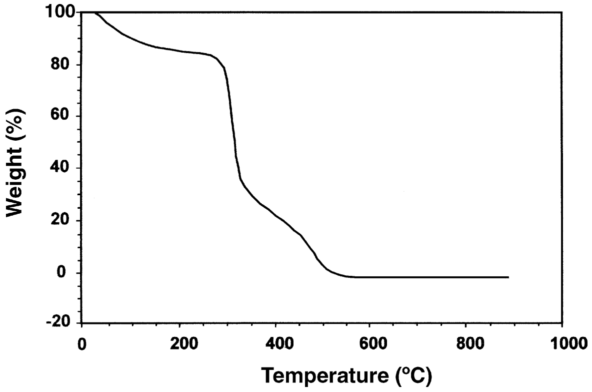

Fig. 3. TGA diagram of wheat particles.

Fig. 3 shows TGA diagram of wheat particles. Wheat particles undergo thermal decomposition leaving negligible char residue which makes it a suitable candidate as pore former. Decomposition of wheat particle took place in three stages; slow decomposition up to 275 °C with a weight loss of 22%, fast decomposition with a weight loss of 50% in the temperature range 275–350 °C and slow decomposition with a weight loss of 18% in the temperature range 350–550 °C. Wheat particles in green alumina samples also showed the same decomposition pattern. Since 82% of the wheat particles were removed below 350 °C, a slow heating rate of 0.5 °C/min is used in this temperature range for binder removal from the green bodies.

The bodies did not show any deformation or cracks during burnout of pore former and sintering. As expected, sintering shrinkage of the samples increases as the amount of wheat particle in the green body increases. The sample showed isotropic sintering shrinkage and was observed in the range 42.6–47.7 vol%. Porosity of the samples increases as the amount of pore former increases. Porosity of the samples prepared from slurry compositions from A to D is in the range 67–76.7%, respectively. Sintering shrinkage and porosity of the samples prepared from various slurry compositions is given in Table 2.

Fig. 4a–d shows the SEM microstructure of porous alumina samples prepared from slurry compositions A, B, C and D, respectively. The microstructures show two types of pores; larger pores having sizes in the range from 200 to 800 μm and smaller pores having size less than 20 μm. The smaller pores are uniformly distributed throughout the struts and cell walls of the larger pores. The separation between large pore decreases as the pore former content in the slurry increases. The smaller pores are due to wheat particle fragments generated during mixing of the slurry.

It is well known that the strength of the porous ceramics decreases with increasing porosity [29]. Diametrical compressive strength of porous alumina samples prepared by the present method decreases from 5.9 to 2.0 MPa when porosity increases

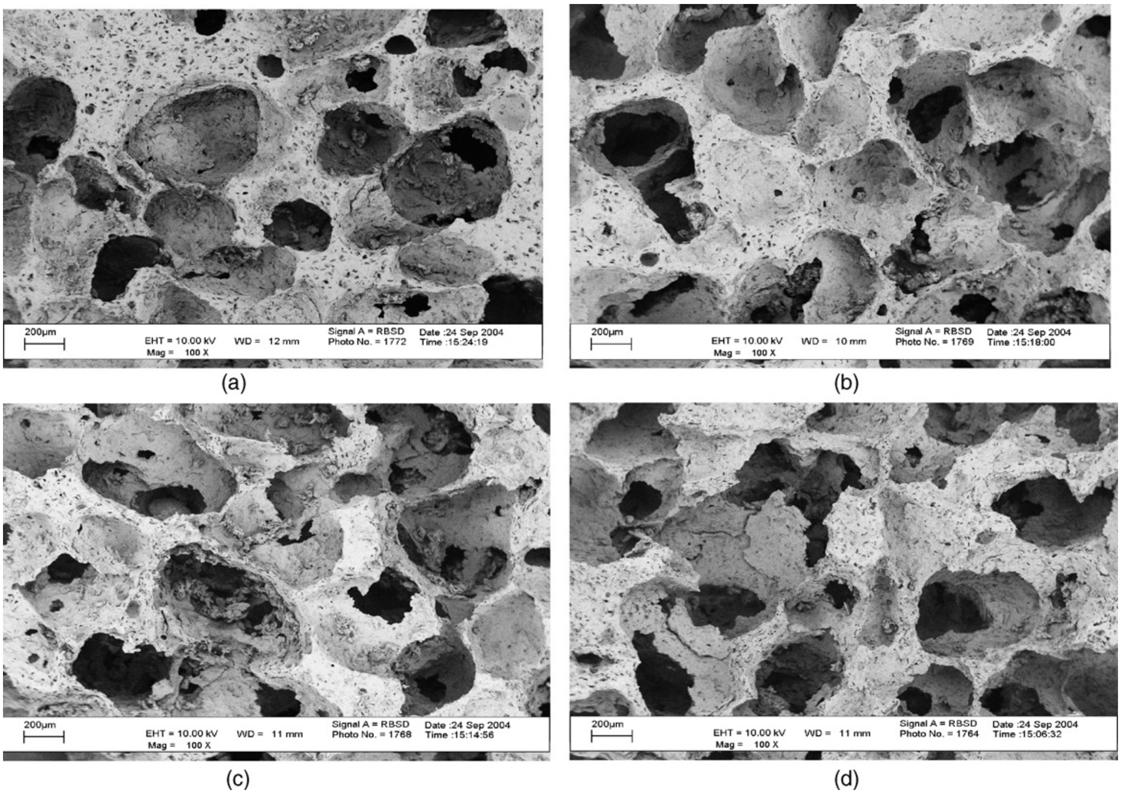

Fig. 4. SEM microstructure of the porous alumina samples prepared from various slurry compositions: A (a), B (b), C (c), and D (d).

from 67 to 76.7%. Strength values of the porous alumina samples prepared from various slurry compositions is given in Table 2. Fig. 5 shows a photograph of sintered porous alumina bodies. The slots and hole were made in the green state by grinding and drilling process.

In starch consolidation process developed by Lyckfeldt and Ferreira [26] aqueous alumina powder suspensions containing starch granules undergo gelation on heating at or above 80 °C. However, the alumina slurries containing wheat particles found gelling at room temperature in few hours. This could be due to higher rate of water absorption by wheat particles compared to starch granules. Rectangular and cylindrical bodies obtained by gelation of the slurries in open moulds at room temperature could be removed from the mould within 3 h after casting. However, the gelled bodies did not have adequate handling strength. The gelled bodies attained handling strength after

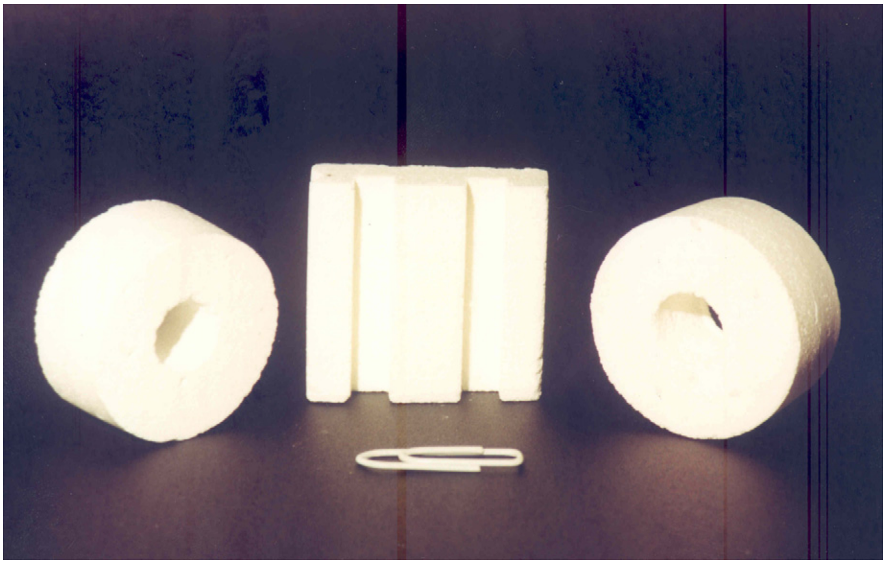

Fig. 5. Photograph of sintered porous alumina bodies showing slots made by grinding and hole made by drilling in the green state.

drying for a period of 24 h at room temperature. Unlike starch consolidation process porous bodies having intricate shapes could not be fabricated with the present process due to high viscosity of the slurry at low shear rate which limits filling of the slurry in moulds with intricate shape. On the other hand, the process is highly suitable for fabrication of simple shapes such as rectangular bricks and cylindrical bodies. Compared to the starch consolidation process which produces porous ceramics with pore size $<50\ \mu m$ the present method is useful for the preparation of porous alumina ceramics with large pores (up to $800\ \mu m$). Further, the process using wheat particle produces maximum porosity of 76.7% compared to <70% by processes reported in literature using starch granules [26].

4. Conclusions

A simple process for preparation of macroporous alumina ceramics from aqueous powder suspensions using wheat particles as gelling and pore forming agent has been demonstrated. Wheat particles incorporated in aqueous alumina slurries rapidly absorb water on heating and transform it into a strong gel. The green bodies prepared have diametrical compressive strength in the range 0.41–0.59 MPa and are amenable to machining operations such as milling, drilling and lathing. Sintered alumina bodies with porosity 67–76.7% and diametrical compressive strength 5.9–2.01 MPa could be prepared. Microstructure showed large ($200–800\ \mu m$) and small ($<20\ \mu m$) pores. Small pores are uniformly distributed in the strut and walls of large pores.

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