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Starch consolidation of alumina: Fabrication and mechanical properties

J. Chandradass[a], Ki Hyeon Kim[a,*], Dong sik Bae[b], K. Prasad[c], G. Balachandar[c],
S. Athisaya Divya[c], M. Balasubramanian[d,*]

[a] Department of Physics, Yeungnam University, Gyeongsan, Gyeongsangbuk-do-712-749, South Korea
[b] School of Nano and Advanced Materials Engineering, Changwon National University, Gyeongnam-641-773, South Korea
[c] Department of Ceramic Technology, Anna University, Chennai-600025, India
[d] Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai-600036, India

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Abstract

A consolidation technique based on gelling property of starch was used to prepare alumina ceramics. Slurry containing alumina powder, dispersant and small amount of starch (2–3.5 wt.% of powder weight) was cast into a nonporous mould and heated to gelation temperature to produce a rigid green body. A defect free green body was obtained and the total linear shrinkage during drying was 2–3% and the green density observed was 64% of theoretical value. After complete drying, ceramic compacts were sintered without debinding operation. Sintered density of 99.4% was achieved after sintering at 1600 °C for 2 h. Flexural strength values of dried and sintered alumina were ∼10 and 247 MPa, respectively. The sintered ceramics showed an extremely dense microstructure.

Keywords: Drying; Sintering; Microstructure; Mechanical properties; Al_2O_3

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1. Introduction

To produce commercial ceramic products, the existing forming methods such as die compaction, slip casting and injection moulding have had limited success because of various problems associated with processing. In dry pressing, a fine ceramic powder is intentionally granulated for free flowing and the variation of the bulk density of powder granules during pressing results in non-uniform powder packing.[1] Similarly, slip casting produces weak green bodies and further machining to engineering shapes becomes impossible.[2] The current injection moulding technology possesses several shortcomings such as prolonged heating for binder burn out, moulding defects, warpage and differential binder removal in thin and thick sections, that limits its use as a complex shape forming method. Based on well-established methods, such as die compaction, slip casting and injection moulding, research is being carried out to develop processes for the direct consolidation of powders.[3]

Gelcasting has established itself for its simplicity and its ability to produce a high degree of homogeneity as well as green body strength, resulting in good machinability. Gelcasting is an advanced ceramic process developed at Oak Ridge National Laboratory (ORNL), USA, by Janney et al. to make complex shaped parts.[4] Gelation in the casting process refers to the formation of a rigid polymeric network that retains the ceramic particles inside. Non-aqueous gelcasting process was first reported in early 1990s[5]; then the same underwent different modifications[6–9] over the years. Much effort has been devoted in recent past to develop aqueous gelcasting process because of the obvious health, safety and environmental benefits. This has increased the interest on searching for gelling agents compatible with aqueous media. Consequently some fruitful results had been obtained[10–13] with few limitations, for the fabrication of dense ceramics using aqueous gelcasting process.

Consolidation of ceramic parts through binder gelation method has the potential to reduce the cost of shaping procedure. On the other hand, gelling additives provide very strong green bodies that can be easily handled and machined.[14] Besides the chemical gelation by means of catalyst, another approach to ceramic processing is to promote thermal gelation through polymer solution that gelates under suitable temperature conditions.

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* Corresponding authors. Tel.: +82 53 810 2334; fax: +82 53 810 4616.
E-mail addresses: kee1@ynu.ac.krc (K.H. Kim),
mbala@iitm.ac.in (M. Balasubramanian).

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In food industry, the application of gel is so common that ice cream, jelly, bean jelly, pudding and jam are all based on the gelation.[15] Besides these, there are some reports about utilising natural polymer in ceramic forming process, such as gelatine,[16] carrageenan,[17] alginate[18] and silica sol,[19] polysaccharides[20,21] and starch.[14,22]

Starch is widely present as a reserve of carbohydrate in the leaves, stems, roots and fruits of most land plants. Commercial sources include the seeds of cereal grains (corn, sorghum, wheat and rice), certain roots (potato, tapioca or cassava and arrow root) and the pith of the sago palm. Starch is used as a component and processing aid in the manufacture of adhesives, textiles, paper, food, pharmaceuticals and building materials. The wide use of this natural polymeric material is based on its thickening, gelling, adhesive and film-forming capabilities. These properties can be modified by chemical, physical or enzyme treatment to obtain optimum characteristics for each specific application.[23]

Alves et al.[22] and Lyckfeldt and Ferreira[14] reported that porous cordierite and alumina bodies can be formed by starch consolidation method based on the properties of starch in water. In the present work, formation of dense alumina bodies based on the gelling capability of starch granules is studied. When an aqueous suspension of ceramic powder and starch are heated up to 60–80 °C, the starch particles swell due to water uptake. The amount of water available for flowing gradually decreases, causing the ceramic particles stick together and consequently, consolidate into a solid body. The disrupted crystalline regions of starch granules adsorb at the surface of ceramic particles, acting like a binder and improve the strength of the consolidated body. This enables demoulding prior to drying. Besides the favourable gelling properties, starch is environmentally friendly, easy to burn out and very cheap.

2. Experimental procedure

Alumina powder (A1000, HINDALCO) of 99.8% purity, BET surface area of 5.1 m^2/g and average particle size of 0.4 μm is used as the starting material. Chemical analysis of the alumina powder is given in Table 1.

The flow chart for the preparation of ceramic body is shown in Fig. 1. Ceramic slurry is prepared by introducing starch (Food grade, fine rice flour) as gelling agent and ceramic powder into distilled water. To prevent the agglomeration of ceramic powder, a dispersant (Darvan C) is added and the slurry is well mixed using magnetic stirrer and further mixed in ball mill for 48 h. For the fabrication of monolithic ceramics, solid loading of 56 or 60 vol.% is maintained in the ceramic slurry. The amount of gelling agent (starch) is varied from 2 to 3.5 wt.% and the amount of dispersant is kept constant at 1.1 ml for 100 g of alumina powder. The slurry is transferred to a metal, plastic or glass container, which is coated with a known releasing agent, such as wax. The containers are tapped well to remove the maximum extent of trapped air bubbles from the cast. The mould is kept inside an air oven for 1 h, which is maintained at 70 °C. In order to retain water in the slurry until the completion of gelation, the temperature is maintained at 70 °C. Cast specimens are released from the container after cooling to room temperature. The gel cast monolithic ceramics are dried at 120 °C for 2 h to ensure that the specimens are dried-up well to be nearly free of water. The dried specimens are sintered in a high temperature furnace (Nabertherm HT 04/17) under normal atmospheric conditions. The specimens are first heated to 600 °C at a rate of 3 °C/min and then to 1600 °C at a rate of 5 °C/min. All the specimens are soaked at this temperature for 2 h to obtain dense ceramics.

Table 1
Chemical analysis of alumina powder.

Oxides	Wt.%
Al_2O_3	99.8
Na_2O	0.06
Fe_2O_3	0.02
MgO	0.03
SiO_2	0.03
CaO	0.02

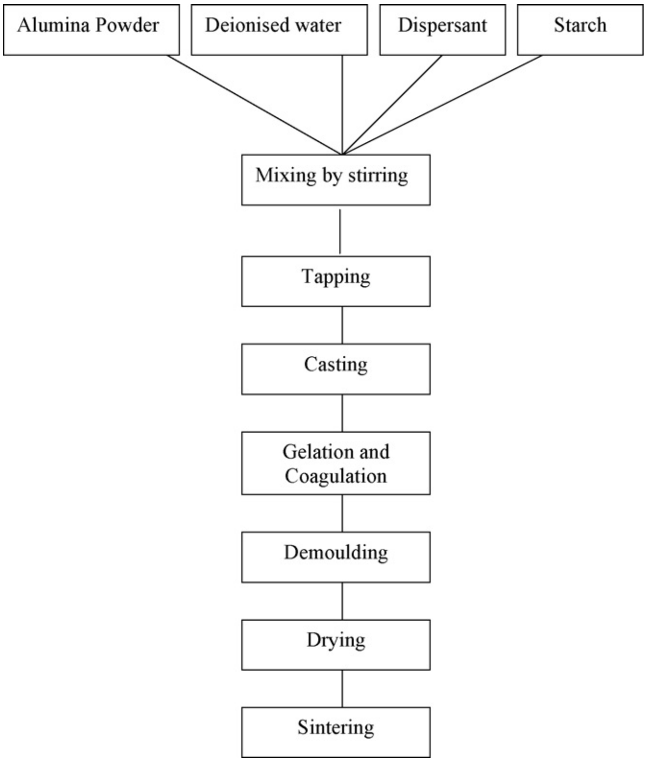

Fig. 1. Flow chart of starch consolidation process to prepare ceramic shapes.

The green and sintered densities were measured by the Archimedes' method using water as immersion medium. Percentage of theoretical density for green samples is calculated using the following equation:

$$\frac{\rho_o}{v_A \rho_A + v_s \rho_s} 100$$

where ρ_o is the obtained density, v_A the volume fraction of alumina, v_s the volume fraction of starch, ρ_A the theoretical density of alumina, ρ_s the theoretical density of starch.

Theoretical density of starch is 1.39 g/cm^3 and alumina is 3.98 g/cm^3. For the sintered samples, volume fraction of alu-

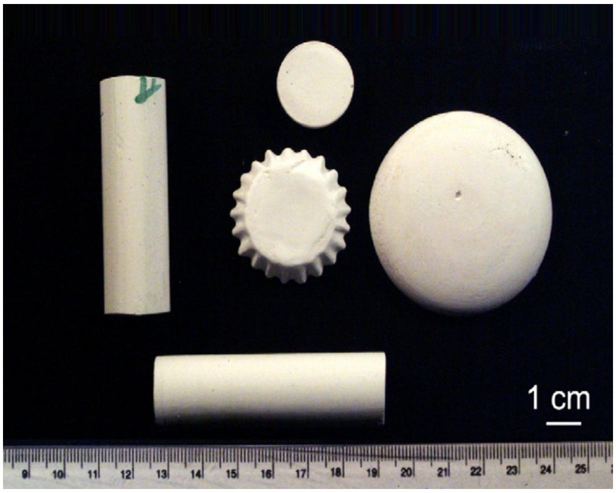

Fig. 2. Conventional photograph of dried alumina specimens.

mina is taken as 1 and volume fraction of starch is taken as 0. Room temperature mechanical strength of green and sintered samples is determined by three-point flexure test with a span length of 30 mm (crosshead speed of 0.5 mm/min) using universal testing machine (Instron 4301). The dried and sintered samples are mounted on copper stub and gold coated in a sputter coater. The microstructure of these gold-coated samples is observed using scanning electron microscope (Quanta 200, FEI, Oregon, USA).

3. Results and discussion

Starch is composed of semi-crystalline particles of A chains and exterior B chains of amylose and amylopectin.[24] The amorphous region consists of free amylose, lipid-complexed amylose (L-AM) and α-1,6 branches of amylopectin.[25] When starch suspension is heated, the particle absorbs water and swell, due to dissolution of amylose molecules and destruction of the crystalline region. According to previous findings,[26] the starch gel is composed of the dispersed swollen starch particles embedded in a continuous three-dimensional network created by the dissolved amylose. At an early stage between 55 and 57 °C, amylose molecules dissolve from the swollen starch particles and the suspension transforms into sol.[27] Between 57 and 62 °C, closely packed network of swollen starch granules[28] forms by sol to gel transition, that is, a three-dimensional gel network is constructed from the amylose, reinforced by strong interaction among the swollen starch particles[29]. Between 62 and 66 °C, the gel structure is destroyed.[28] The destruction was probably due to the melting of the crystalline region remaining in the starch granule, which deformed and loosened the particles.[30] Between 66 and 70 °C, the leached low molecular weight amylopectin interacted with amylose matrix to strengthen the continuous phase. However, the dispersed phase becomes softer due to continuing dissolution of amylopectin. Beyond 70 °C, the gels appeared to be sticky and sensitive to strain.[27]

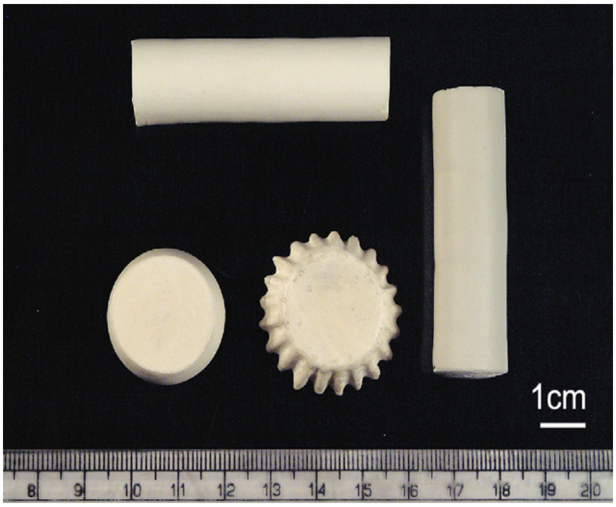

Fig. 3. Conventional photograph of sintered alumina specimens.

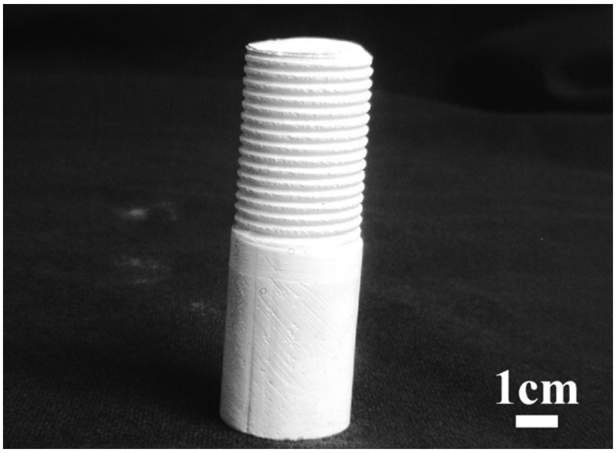

Fig. 4. Machined green specimen.

Starch particles will swell by water uptake, when a slurry containing ceramic powder and starch is heated at 60–80 °C. Swelling removes water from the slurry causing the ceramic particles stick together and consequently, consolidate into a solid body. As starch granules or particles swell, they also act as a binder adding strength to the consolidated body that enables demoulding prior to drying.[31]

The green body shows a linear shrinkage of 2–3% during drying. So, this technique can be used for producing near net shape ceramic body. Various shapes of green and sintered alumina bodies prepared by this technique are shown in Figs. 2 and 3. A machined green body is shown in Fig. 4.

Table 2
Density of dried and sintered alumina specimens.

Sample	Green density (%TD)		Sintered density (%TD)	
	56 vol.% alumina	60 vol.% alumina	56 vol.% alumina	60 vol.% alumina
2.0 wt.% starch	53.2	59.7	96.4	98.9
2.5 wt.% starch	55.4	63.9	97.4	99.4
3.0 wt.% starch	54.1	56.9	96.6	98.9
3.5 wt.% starch	52.9	52.4	95.9	98.1

Table 3
Flexural strength of dried and sintered alumina specimens.

Sample	Flexural strength of green samples (MPa)		Flexural strength of sintered samples (MPa)	
	56 vol.% alumina	60 vol.% alumina	56 vol.% alumina	60 vol.% alumina
2.0 wt.% starch	5 ± 0.2	9 ± 0.7	197 ± 7	217 ± 13
2.5 wt.% starch	6 ± 0.4	10 ± 0.5	201 ± 6	247 ± 10
3.0 wt.% starch	5 ± 0.7	8 ± 0.5	200 ± 4	209 ± 7
3.5 wt.% starch	5 ± 0.5	7 ± 0.8	196 ± 7	197 ± 9

The green and sintered density values of specimens containing 56 and 60 vol.% alumina powder are given in Table 2. The green density is highest for specimen prepared using 60 vol.% alumina powder and 2.5 wt.% starch. The highest density achieved for green body in the present study is ∼64% of theoretical density. The green density is low at higher starch contents. Ceramics made by this method have linear shrinkage varying from 13 to 15% during sintering and attain a maximum density of 99.4% of theoretical density for the sample prepared using slurry containing 60 vol.% alumina powders. An increasing number of particles in suspension leads to their closer mutual approach and hinders particle segregation phenomena. Moreover, there exists the possibility of starch to form polymer bridges by adsorption on adjacent alumina particle. All these factors can account for the increase in green strength. Flexural strength values of dried and sintered specimens are given in Table 3. In general, two factors affect the strength of the materials: the nature of bonding and the presence of defects, such as pores, which act as stress concentrators. In the green body, the ceramic particles are occluded in the globular polymer matrix. Therefore, the dry strength is not related to porosity and should be decided by the nature of the gel bonding. The highest flexural strength was obtained for 60 vol.% alumina powder containing 2.5 wt.% starch. Flexural strength is lower for the specimens prepared with starch content of more than 2.5 wt.%. This may be accounted by the inhomogeneous slurry mixing or the presence of agglomerates or flocculation resulting from the higher viscosity.[16] The flocculation occurring in the suspension may

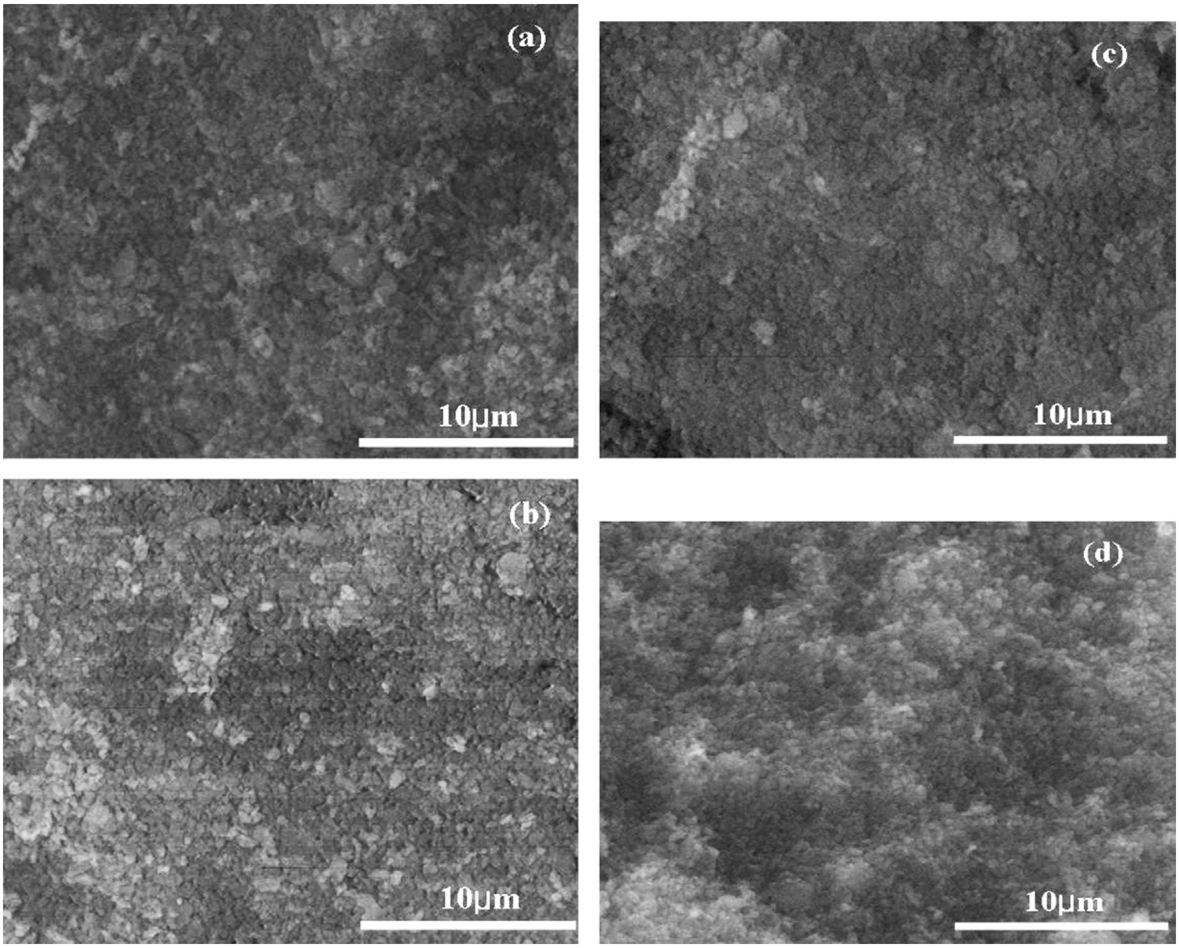

Fig. 5. SEM micrographs of dried alumina specimens prepared with (a) 2 wt.% starch; (b) 2.5 wt.% starch; (c) 3.0 wt.% starch; (d) 3.5 wt.% starch

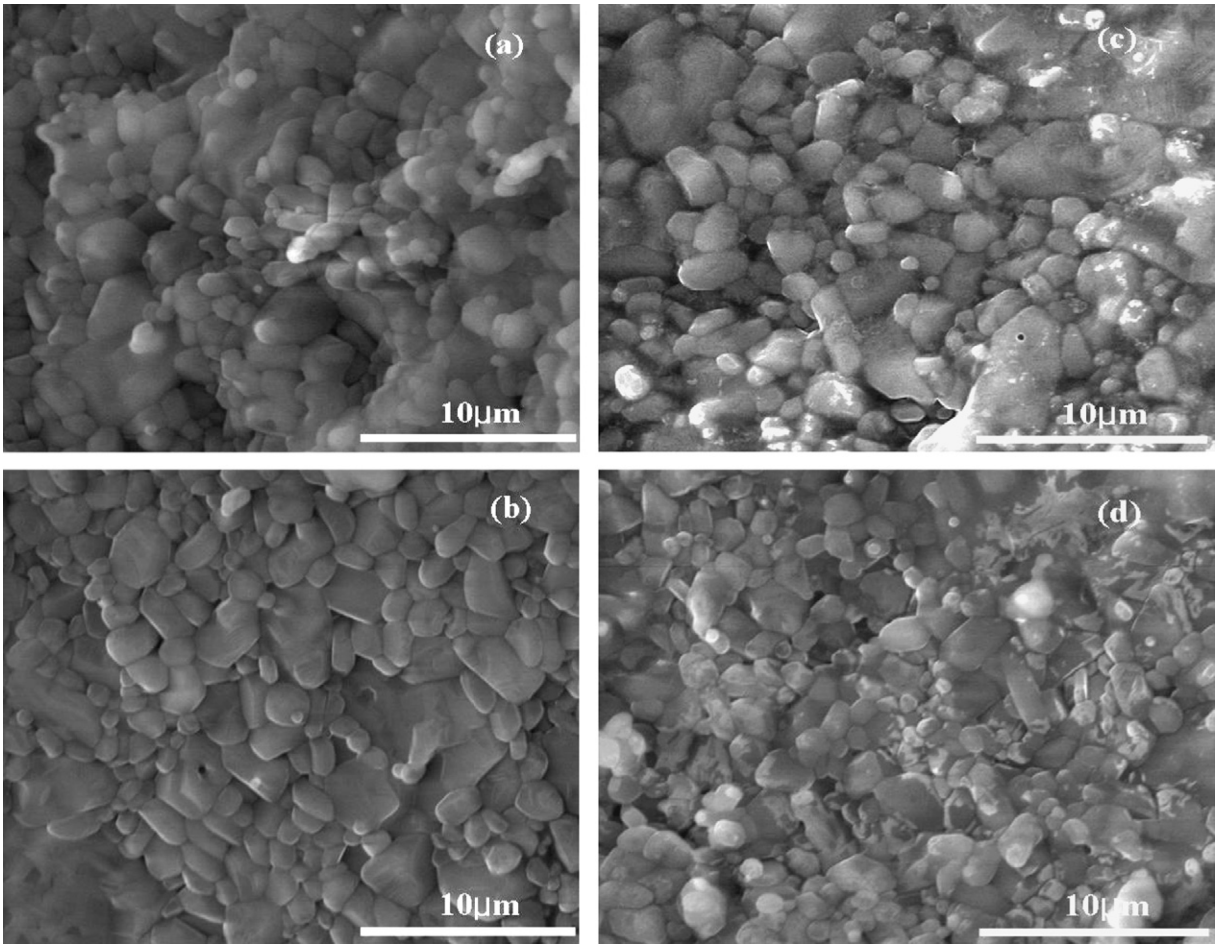

Fig. 6. SEM micrographs of sintered alumina specimens prepared using (a) 2 wt.% starch; (b) 2.5 wt.% starch; (c) 3.0 wt.% starch; (d) 3.5 wt.% starch.

act as sources of flaws in the sintered compact.[28] The highest flexural strength values of dried and sintered gel cast specimen are 10 and 247 MPa, respectively. Based on the fluidity of the slurry and the strength of the green body, 2.5–3 wt.% starch is better suitable for preparing slurry containing 56 or 60 vol.% alumina.

The microstructure of green specimens is shown in Fig. 5. Pores are fine and uniform in the specimens prepared with 2.5 wt.% starch, whereas the pores are non-uniform in the other specimens. The microstructure of sintered specimens is shown in Fig. 6. Uniform and fine grains of size 2 μm with occasionally larger grains of size ~3.5 μm are present in the sample prepared from the slurry containing 60 vol.% alumina and 2.5 wt.% starch. Two important features can be highlighted from these micrographs. Uniform packing of ceramic particles without any agglomeration or defect such as macro/micro-pores is one of the salient features and is essential in the fabrication of monolithic ceramics to obtain defect free specimens after sintering, because these defects would be retained after sintering and propagate during loading of the sintered material. Origin of agglomerates can be due to incomplete dispersion of ceramic particle or incomplete dissolution of gelling agent in the solvent medium. Chumnanklang et al.[32] reported that for higher starch content, the gelled starch occupies a larger space between the particles. After the binder burn out step, the larger pores cannot be eliminated and hence it results in a higher porosity ceramic. This may be the reason for the lower density and flexural strength, when the specimens are prepared with starch content of more than 2.5 wt.%.

4. Conclusions

- Suitable starch content for castable slurry with 56 and 60 vol.% alumina is 2–3.5 wt.% (based on water).
- Green bodies with precise size and relatively smooth surface can be obtained by starch consolidation. The green bodies are having high density and flexural strength.
- Sintered samples prepared from the slurry containing 2.5 wt.% starch have the highest density and flexural strength.

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