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Effect of additives on the microstructure of porous alumina

Sarama Bhattacharjee*, Laxmidhar Besra, Bimal P. Singh

Regional Research Laboratory, Bhubaneswar 751013, India

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Abstract

Protein forming, a direct consolidation technique for shaping of powders into a rigid body, use globular protein as gelling agent, which makes the process environment friendly. The present paper combines foaming and gelling capabilities of globular protein (albumin) along with starch to consolidate the ceramic bodies to develop porous structure based on alumina. The effect of albumin and starch on the gel strength, rheological properties of alumina slurry as well as the microstructure of final structure were studied in detail. It has been observed, that albumin which gels by forming strong polymer network dominates the gel properties, and thereby the strength of the consolidated green bodies, whereas starch, being insoluble in water at room temperature, increases the viscosity of slurry, but increases stability of foamed slurry. Also starch acts as pore former to introduce connectivity between pores and hence increases open porosity. Hence, by controlling albumin and starch ratio in the slurry one can control the microstructural developments in the cast body to obtain the desired micro-structure.

Keywords: Porous body; Al_2O_3; Suspensions; Porosity; Microstructure

1. Introduction

For successful application of advanced ceramic materials, the control of the microstructure and the tailoring of related physical properties such as mechanical strength, fracture toughness as well as thermal shock and wear resistance are of crucial importance. To achieve optimal sintering conditions, adequate materials properties and dimensional tolerances, dense and homogeneous packing of powders as well as evenly distributed additives are required. New forming processes are constantly being evolved to meet these requirements so as to obtain a cheaper, environment friendly and reliable processing of ceramics.

Several process concepts based on ceramic slurry have been introduced in Direct Consolidation techniques,[1–9] where it is required to have a well dispersed suspension of high solids loading with reasonably low viscosity to facilitate the mould filling process. In these methods, the particle structure of the ceramic slips is consolidated without powder compaction or removal of liquid. One of the concepts, protein forming,[6] uses functional properties, such as gelation, of globular protein (e.g. egg albumin) to consolidate the ceramic bodies. However, globular proteins also show surface active properties, for example, it is known that in aqueous solution egg albumin proteins get adsorbed at air/water interfaces, and unfolded, which increases hydrophobicity and hence formation of foam. Agitation of protein solution further increases foaming capacity by breaking the di-sulfides bonds and increasing the flexibility of proteins to unfold. Gelling and foaming capabilities of globular protein have been exploited by Dhara et al.[10] to develop foamed ceramic. Use of protein/starch as gel/ thickening agent is well known in the food industry. It has been reported[11] that simultaneous use of whey protein and cassava starch improves gel strength, where starch granules swell first by absorbing water, thereby concentrating the protein in the solution that gels later. In fact, starch has been used successfully[4] as simultaneous consolidator of ceramic body as well as pore former to develop porous structure. Different functional properties, such as, thickening, binder, gelling capabilities have been exploited to prepare porous bodies. In both the egg albumin and starch, the gelling is induced thermally and occurs around the same temperature ranges (60–90 °C) in aqueous solution. In this paper, we exploit these properties of albumin and starch and design microporous alumina ceramics by combining both foaming and gelling characteristics of albumin and starch consolidation. We study in detail the effect of differ-

* Corresponding author. Tel.: +91 674 2581635; fax: +91 674 2581637.
E-mail address: saberip@yahoo.com (S. Bhattacharjee).

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ent additives on the rheological properties of the slurry and on the final microstructure.

2. Experimental

2.1. Materials

High pure α-alumina (CT-300 SG) obtained from ALCOA, India, has been used for this investigation. The average particle size and the BET surface area of the powder used are 0.7 μm and 7.0 m^2/g, respectively. The dispersant used was an ammonium salt of polymethacrylic acid, supplied by M/S, R.T. Vanderbilt Co., Norwalk, CT, USA and is available commercially with the trade name Darvan C. It has an average molecular weight of 10,000–16,000 g/mol. It is a 25% (w/v) aqueous solution with an active matter percentage of about 35%. Dry albumin flake, purchased from M/s BDH Chemicals, Poole, UK, and soluble potato starch from M/s Qualigens Fine Chemicals, Mumbai, India, have been used for these studies. Other reagents employed are of analytical grade and have been used without any further purification. In all the experiments deionized water has been used for preparation of suspension.

2.2. Preparation of albumin and albumin/starch solution

Albumin solution of various concentrations in aqueous medium have been prepared by stirring the solution for 1 h at room temperature to allow the protein to dissolve properly. On the other hand, starch is insoluble in water at room temperature. Hence, starch suspensions of different pre-determined wt% have been prepared in albumin solution, which were further subjected to rheological studies.

2.3. Sedimentation studies

Stability of foam in the alumina slurry was monitored by conventional sedimentation method by using graduated glass cylinders. Fifty millilitres of 10 vol% alumina slurry containing 5 wt% albumin based on water phase and 50 ml of 10 vol% alumina slurry containing 5 wt% albumin and 5 wt% starch (based on water phase) were prepared. Foam was generated either by stirring or by tumbling for 1 h. The contents were then transferred to graduated cylinders and allowed to stand undisturbed. An interface separating the clear supernatant liquid at the top and the turbid suspension at the bottom could be seen descending slowly with time. The dispersion volumes (defined as the volume of the dispersion/supernatant interface) and sediment height were measured at 0, 1, 12, 24, 36 h.

2.4. Preparation of alumina slurry

To prepare slurry of desired vol% and solid loading, required amount of alumina was added stepwise to a fixed volume of premix solution containing optimum dosage of Darvan C (established earlier and published elsewhere[12]) in de-ionized water followed by milling for 12 h in a roller mill containing zirconia balls. To have effective mixing two different sizes of zirconia balls were employed.

After milling, varying amounts (5–30 wt%, based on water phase) of albumin and albumin/starch solution were added to the slurry and mixed thoroughly. After 1 h of mixing, the slurry was subjected to de-airetion to remove undesired entrapped bubbles. The slurry was then stirred/tumbled for pre-determined time before subjecting it to rheological measurements to ascertain the effects of bubbles on gelling kinetics.

2.5. Rheological measurement

Fluidity of slurry was determined by measuring apparent viscosity at a steady shear rate range 0–1000 s^{-1} using parallel plate geometry (Paar-physica rheometer model: MCR-300) with a gap of 1 mm at a constant temperature of 25 °C. Before each measurement, pre-shearing was done for each sample for 1 min at highest shear rate followed by a rest period of 2 min.

To characterize the gelling behaviour of albumin and albumin/starch combination, small amplitude dynamic oscillatory measurement were performed at constant frequency of 1 Hz and constant strain (0.1%) using parallel plate geometry. The temperature of the cell was varied at continuous ramp from 25 to 80 °C, during which storage modulus (G'), the elastic component of the complex shear modulus ($G^* = G' + G''$) was measured. The measurement was performed at interval of 5 s. The storage modulus (G') value can provide a valuable insight regarding the gelling characteristics of the suspension. A high value of G' signifies a more solid like behaviour whereas a high value of loss modulus (G'') represent a more liquid-like behaviour. Hence G' is expected to increase upon gelation.

2.6. Fabrication of ceramic bodies

For casting ceramic bodies, slurries containing a suitable volume percent of solid, foaming agent (egg albumin) and starch were first stirred/ tumbled for fixed duration of time. The concentration of additive (albumin and starch) was varied from 5 to 30 wt% based on water phase, while albumin to starch ratio was varied through 0.5:1, 1:1, 1.5:1, 2:1 to 6:1. The slurry was gelled by promoting formation of a relatively rigid cross-linked polymer network by heating it at 60–80 °C.

A wide range of shapes were formed using various plastic moulds. The slips were poured in the mould and kept in a preheated oven at 45 °C and then the temperature of the oven was raised slowly to 80 °C in 2.5 h time. In some cases, the moulds were covered to minimise the loss of solvent during solidification process. After consolidation, cast bodies were cooled to room temperature and de-moulded. Complete drying was then conducted at room temperature for 24 h and subsequently at 120 °C for 12 h. Burn out of the organics was then conducted by heating the cast body in air at 1 °C/min to 600 °C and soaked there for 2 h. This was followed by sintering at 1550 °C for 2 h to obtain hard and strong ceramic body. Some products were pre-sintered at 1000 °C to find out the density after binder burnout.

The densities of the consolidated bodies after binder burnout and after sintering were determined using Archimedes principle using ASTM standard C 20–00 and correlated with the amount of porosity in the body. The microstructure of the final product were evaluated by scanning electron microscopy (JEOL, JSM1600).

3. Results and discussion

3.1. Rheological studies of albumin and starch aqueous solution

Gelling behaviour of different weight percent of albumin solution, starch suspension and albumin and starch solution at different weight ratios have been shown in Figs. 1 and 2. Pure albumin solution shows distinct gelling (storage modulus G' increases sharply from $\sim 10^{-1}$ to 10^4 Pa) at temperature between 50 and 60 °C, depending on the concentration of albumin (Fig. 1a). Higher the concentration of albumin, lower is the gelling temperature. This is understandable, since albumin gels by denaturation followed by intermolecular interactions to form thermo-irreversible polymer network through formation of hydrogen bonds. Higher the concentration, greater is the probability to have a protein molecule as nearest neighbour to interact. Fig. 1b shows the gelling behaviour of starch suspension. The nature of gelling is same as albumin, however, starch suspension shows comparatively prolonged gelling and much lower rise of storage modulus (from 0.5 to 3.5 Pa), and hence much lower gel strength. During gelling of albumin, strong intermolecular hydrogen bonds are formed between albumin protein molecules to have a strong irreversible polymer network, whereas in starch suspension, at the onset of gelling, starch molecules absorb large amount of water and swell imparting a substantial increase in viscosity[13] and hence a weak gel former compared to albumin. Fig. 2 shows the gelling kinetics with varying ratios of albumin and starch, keeping total solid (albumin + starch) at 5 wt%. Below the gelling point, the albumin solution behaves like a perfect liquid as evident by a very low value of G' compared to solutions containing starch. It is also clearly evident that initiation of gelling occurs at lowest temperature for pure albumin solution compared to any of the albumin/starch mixed solution. As expected, with decrease in the albumin content in the albumin/starch mixed solution, the initiation of gelling is shifted towards higher temperature. But at the same time, it is characterised by lower G' values compared to pure albumin which suggests that the gel strengths of mixed solution are lower than those of pure albumin.

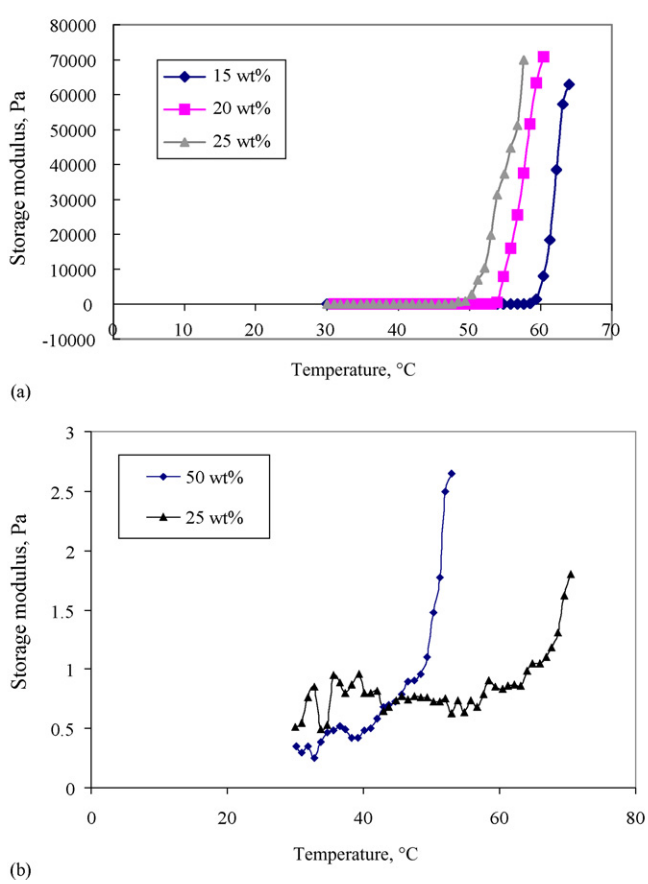

Fig. 1. (a) Gelling kinetics of different wt% of albumin slurry. (b) Gelling kinetics of different wt% loading of starch solution.

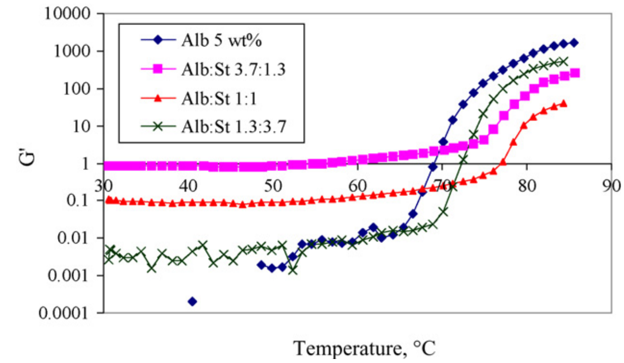

Fig. 2. Gelling characteristics of albumin and starch at different concentration ratio in absence of any powder (total additive content 5 wt%).

3.2. Rheological studies of alumina slurry with additives

Fig. 3(a) shows the flow curve of alumina slurry (45 vol%) with fixed amount of albumin (5 wt% based on water phase) but varying amount of starch. For each of the compositions studied, slurries exhibit shear thinning behaviour, i.e., apparent viscosity decreases with shear rate. As the starch content in the slurry increases, the average apparent viscosity also increases, because of increase in total solid content. Fig. 3(b) shows the flow behaviour of alumina slurry (45 vol%) with addition of albumin and starch at same ratio (2:1) with different total albumin and starch (7.5 and 5 wt%, respectively) content. At lower amount of albumin and starch addition, the slurry behaviour is almost Newtonian, i.e., the slurry viscosity is independent of shear rate.

Fig. 4 show the gelling kinetics of 45 vol% alumina slurry containing albumin and albumin and starch at 2:1 ratio. Solid curve represent gelling of slurry with albumin, which was subjected to de-airing to remove air bubbles, whereas dashed curve depicts gelling behaviour of same slurry but with presence of foam. Both the slurry shows sharp and distinct gelling behaviour

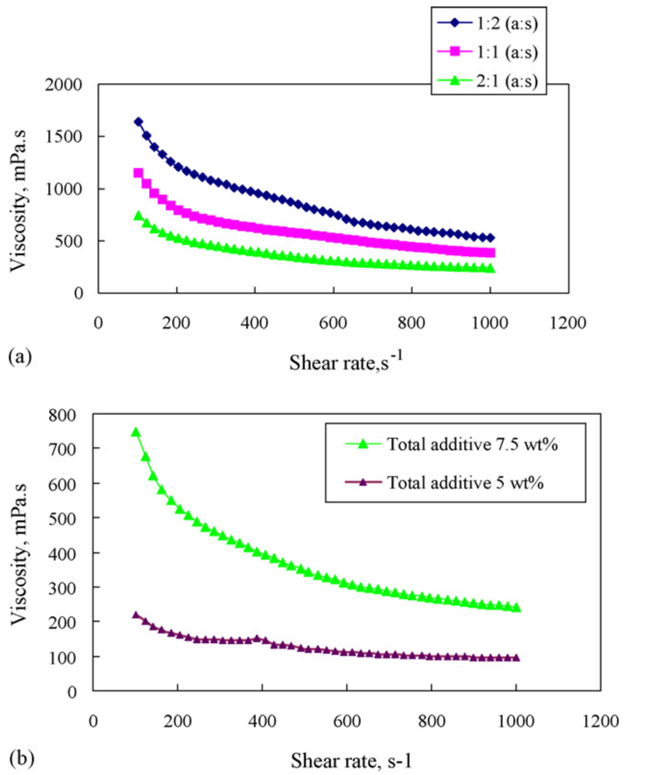

Fig. 3. (a) Flow curve behaviour of 45 vol% alumina slurry with different ratios of albumin and starch (albumin content 10 wt% based on water phase). (b) Flow curve behaviour of 45 vol% alumina slurry with different total additive content (albumin and starch ratio at 2:1).

at a temperature around 40 °C; however, in case of foamed slurry, after gelling, G° stabilises at comparatively lower value, showing inferior strength of the gel compared to the slurry without foam. It is also interesting to note that though the slurry contains 5 wt% albumin compared to the water phase, it gels at much lower temperature compared to the gelling of pure albumin solution at the same concentration. In the same figure thin solid curve represents the gelling of alumina slurry with albumin and starch in presence of foam. As discussed earlier, presence of starch prolongs the gelling process. It can be seen from the figure that presence of both the albumin and starch further improves the gel strength, since slurry without foam and slurry with foam having starch have comparable G' value. At the onset of the gelling, starch reduces the water volume by swelling, therby consolidate the ceramic particles. This increases the concentration of albumin in the remaining water phase, which simultaneously gels by forming the strong polymer network and consequently gel strength improves.

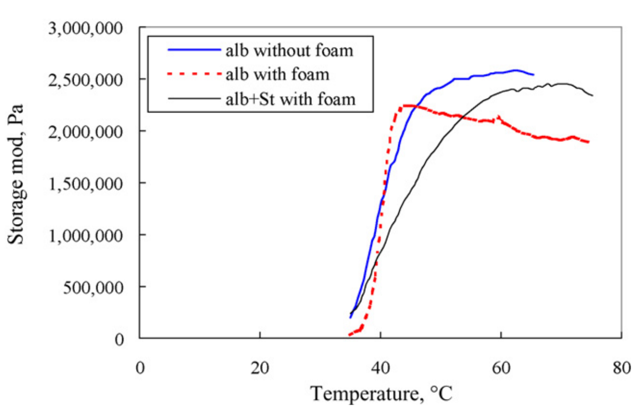

Fig. 4. Gelling kinetics of alumna slurry (45 vol%) with and without foam.

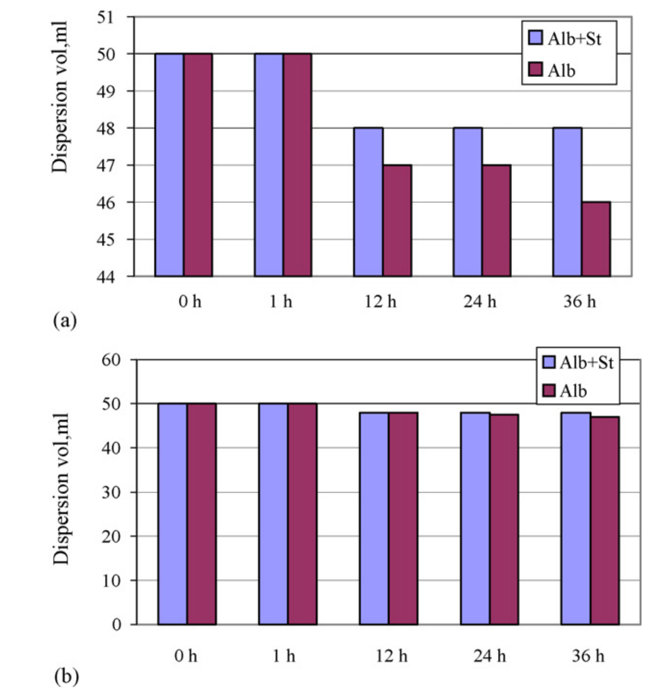

Fig. 5. (a) Sedimentation studies of 10 vol% tumbled alumina slurry with additives. (b) Sedimentation studies of 10 vol% stirred alumina slurry with additives.

3.3. Sedimentation studies

Fig. 5a and b show the sedimentation behaviour of alumina slurry with albumin and albumin with starch, respectively, where the slurries were stirred and tumbled respectively for fixed duration of time. Both the stirred slurry shows better stability with time. On the other hand, in both the cases of stirred and tumble slurry, the presence of starch improves the stability.

3.4. Effect of additives on the microstructure of porous sintered alumina bodies

Experiments were conducted with 45 vol% alumina slurry, where additive (albumin and starch) content in the slurry varied from 5 to 30 wt% based on water phase, whereas albumin:starch ratio was varied from 1:2 to 6:1. Fig. 6a–c show the typical micro-structure of sintered porous alumina bodies cast at different albumin starch ratio. At higher concentration of starch, distribution of pores are non-uniform (Fig. 6a), which reduces as the starch concentration decreases further. This is due to the fact that addition of starch in the slurry increases the viscosity (Fig. 3a), which hinders the uniform generation of bubbles in the slurry.

Total porosity in the structure depends on the amount of bubbles that can be generated and subsequently frozen to get the

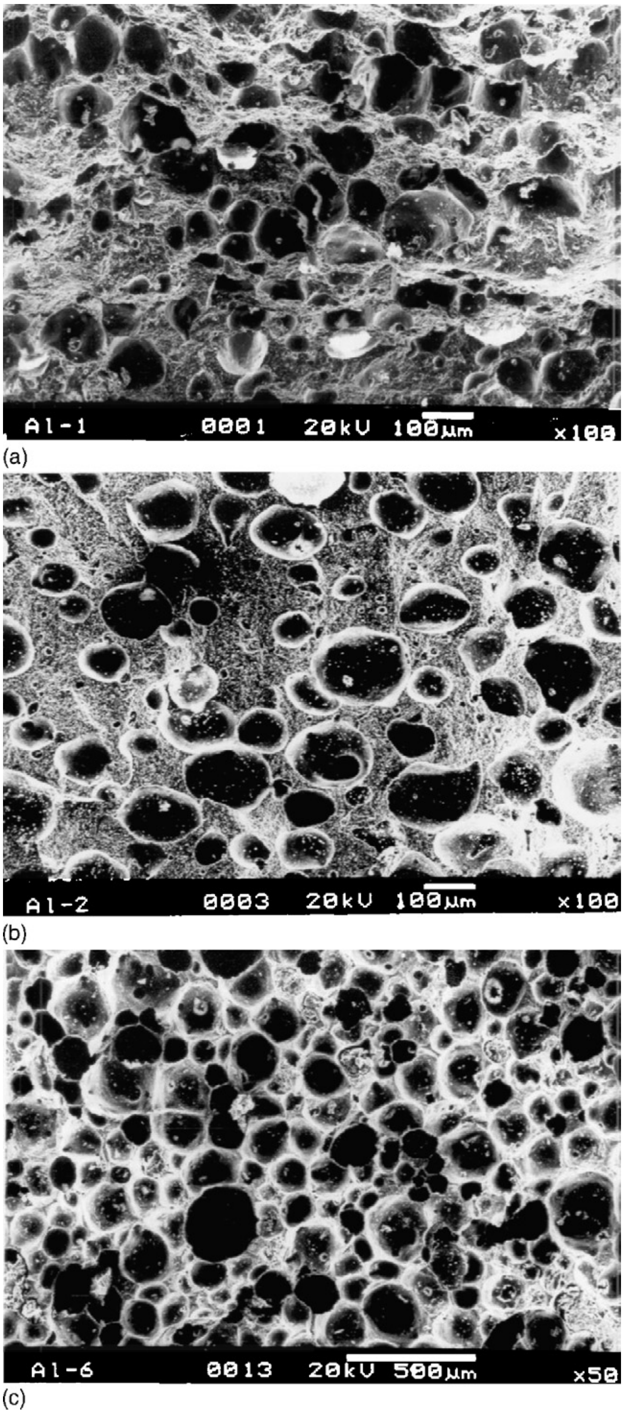

Fig. 6. (a) Microstructure of alumina porous body with albumin starch ratio at 1:2, prepared from 45 vol% alumina slurry containing 20 wt% total additive content based on water phase. (b) Microstructure of alumina porous body with albumin starch ratio at 1:1, prepared from 45 vol% alumina slurry containing 20 wt% total additive content based on water phase. (c) Microstructure of alumina porous body with albumin starch ratio at 2:1, prepared from 45 vol% alumina slurry containing 10 wt% total additive content based on water phase.

structure. This in turns depends on the viscosity of the slurry. This is exemplified in the microstructure Fig. 6a and c, where total porosity increases from ∼50 to 70% as the total additive content decreases from 20 to 10 wt% based on water phase. Increased additive content increases the viscosity of the slurry,

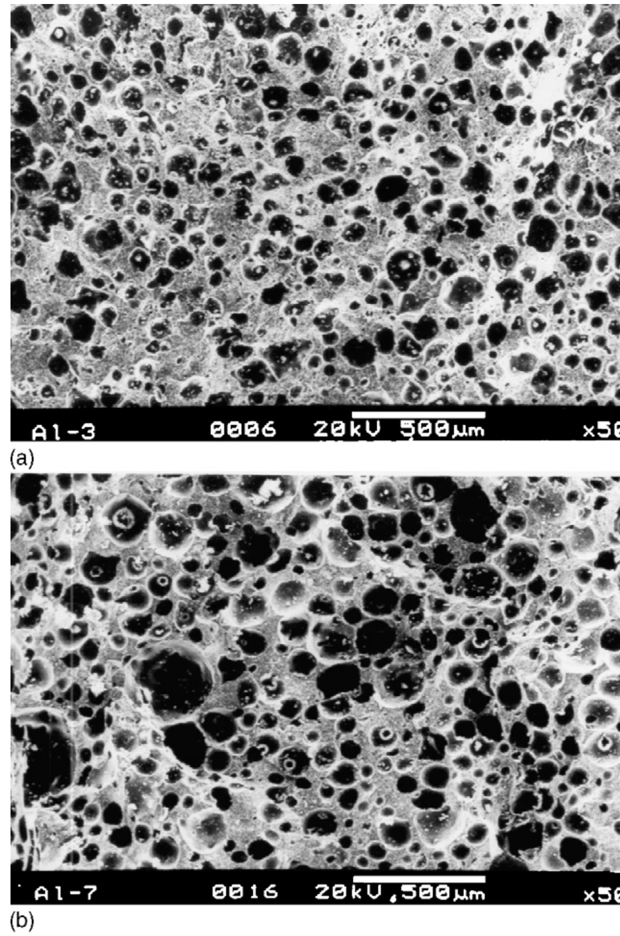

Fig. 7. (a) SEM micrograph of alumina sintered body cast with stirred slurry, prepared from 45 vol% alumina slurry containing 20 wt% total additive content based on water phase, albumin:starch::2:1. (b) SEM micrograph of alumina sintered body cast with tumbled slurry, prepared from 45 vol% alumina slurry containing 20 wt% total additive content based on water phase, albumin:starch::2:1.

which in turn decreases the bubble size generated during foaming. This reduces the pore volume and therefore, the porosity. On the other hand, higher amount of albumin tends to give more closed pores than open. When slurry-containing albumin is stirred, it produces a foamed slurry; if starch is added to this foamed slurry, after burn out, presence of small pores give the connectivity between the bigger pores. Hence, the starch increases the interconnectivity of the pores.

Distribution of pore size also changes with the nature of pore generation. For example, if the slurry is stirred, distribution of pore size is more uniform, whereas tumbled slurry, when cast gives broader distribution of pore size. This is exemplified in the Fig. 7a and b. Fig. 7a represents a microstructure of sintered porous alumina prepared from 45 vol%stirred alumina slurry, with total additive content 20 wt% based on water phase and the albumin and starch ratio at 2:1. The pore size varies from 50 to 150 μm. On the other hand, Fig. 7b shows micro-structure of the sintered porous alumina prepared from the slurry of same composition, but foam was generated by tumbling, where pore size varies from 50 to 300 μm.

4. Conclusions

In direct consolidation technique, to have a control over the final micro-structure, it is necessary to have a flowable slurry so as to achieve proper filling of mould during casting. The green body, after consolidation should have enough strength for easy handling. The paper presents the preparation of alumina porous body by combining both foaming and gelling capabilities of globular protein along with the starch, which further imparts strength in the green body and simultaneously acts as pore former. The paper presents in detail the effect of albumin and starch on the rheological properties of slurry and the final micro-structure developed. Following are the conclusions:

1. Both the albumin solution and starch suspension gel around the same temperature range and gelling temperature reduces as the concentration of respective protein increases. Albumin gels by forming strong intermolecular bond between the proteins, whereas starch gels by water intake, which causes the starch granules to swell. Hence, the gel strength of albumin is much higher than the starch gel strength and in a mixture of two, gelling is dominated by albumin.
2. Flow behaviour of alumina slurry, in presence of both the additives (in the composition range studied), is shear thinning in nature. As the starch content is increased, the average apparent viscosity increases because of the increase in total solid content.
3. Sharp and distinct gelling occurs for alumina slurry containing only albumin. The presence of air bubbles (foam) did not affect the transition temperature. However, after gelling, the storage modulus tend to stabilize comparatively at lower values than the gel without foam, showing inferior strength of the former. In presence of alumina particle, gelling occurs at lower temperature compared to the solution without particle.
4. Simultaneous presence of albumin and starch in the alumina slurry prolongs the gelling process.
5. Sedimentation studies of 10 vol% alumina slurry in presence of albumin and starch, showed that starch improves the stability of foam.
6. Higher content of starch increases viscosity of the slurry and also renders pore distribution of the final micro-structure non-uniform.
7. Total porosity in the final microstructure depends on the viscosity of the slurry, i.e., the ease with which the slurry can be foamed. Presence of albumin tend to make a foamed structure with very little open porosity, while presence of starch, which acts as a pore former increases connectivity.
8. The slurry, which is stirred to generate foam, delivers a porous structure with narrower distribution of pore size compared to the slurry in which the foam was generated by tumbling.

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