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Ceramics International 35 (2009) 1033–1037

CERAMICS INTERNATIONAL

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Gelcasting of alumina nanopowders based on gelation of sodium alginate

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Received 3 January 2008; received in revised form 7 February 2008; accepted 20 April 2008

Abstract

The alumina nanopowder was synthesized via the sol–gel method. θ-Alumina with crystallite size in the range of 25–110 nm was crystallized by calcination of the powder at 900 °C for 1 h. Sodium alginate, a natural innoxious polymer, was applied for in situ forming process of an Al_2O_3 green body, using calcium phosphate as a solidifier agent. Sodium hexa metaphosphate was also utilized as a chelator. Rheological and gelation behaviors of resultant slurry were analyzed. The viscosity of slurries with 15 vol.% alumina and 1.8 vol.% calcium phosphate dispersed by 1 wt.% sodium alginate solution, was less than 800 mPa s. The green bodies from the gelcasting process were dried at room temperature for 36 h and pressureless sintered at 1500 °C for 3 h. A uniform microstructure without huge grain growth was revealed by SEM.

Keywords: D. Alumina; Nanopowder; Gelcasting; Sodium alginate

1. Introduction

In order to shape green bodies from powders, many methods can be used, such as pressing, slip casting, tape casting, injection molding, and gelcasting. Gelcasting is a colloidal forming process to yield ceramics, which achieves in situ solidification of ceramic slurry by the polymerization of monomers. In this process, a ceramic powder is dispersed into a monomer solution and then, after adding catalyst and initiator, it is poured into a mould, polymerized in situ to immobilize the particles in a gelled part, removed from the mold while still wet, and finally dried [1–3].

This forming process has many outstanding merits, such as (1) the strength of the dried green body is so high that it can be machined; (2) it can be used to fabricate ceramic parts of complicated shape; (3) it provides us with the option to use a wide range of mold materials; (4) it makes us capable of manufacturing large parts being comprised of sections with different thicknesses; (5) and it has minimal molding defects. However, the monomer commonly used is acrylamide with neural toxicity. From this point of view, numerous new gelcasting processes with reduced toxicity (such as using of sodium alginate) have been investigated [1,3,4].

Sodium alginate is the sodium salt of alginic acid, a polysaccharide composed of mannuronic and guluronic acids. The acids are natural products produced by the brown sea weeds. Sodium alginate can be dissolved in water at room temperature and then gelled after reacting with divalent metal ions, mainly Ca^{2+}. Therefore, ceramic particles are maintained in a three-dimensional network. The mechanism of cross-linking in alginate gels can be considered in terms of an ‘‘egg-box’’ model involving cooperative bonding of divalent metal ions between aligned polyguluronate ribbons [2,5,6].

Several reports have been presented on the gelcasting of micron and submicron powders by using sodium alginate [1,2,4,6,7]. In this study we investigate the gelcasting of alumina nanopowders by using sodium alginate.

2. Experimental procedure

2.1. Raw materials

The initial alumina nanopowder was prepared via sol–gel [8]. It was then calcined at 900 °C for 1 h and ball milled for

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doi:10.1016/j.ceramint.2008.04.023

48 h. Controllable casting and solidification were carried out by using sodium alginate and calcium phosphate. Na-alginate was utilized as a gelation reagent which dissolves in water at room temperature. Other raw materials used in the present research are as follows: calcium phosphate ($Ca_3(PO_4)_2$) as a solidifier agent, sodium hexa metaphosphate ($(NaPO_3)_6$) as a chelator, ammonium citrate tribasic ($(NH_4)_3C_6H_5O_7$) as a dispersant, and hexandioic acid ($C_6H_{10}O_4$) as an initiator.

2.2. Procedure

The forming process is shown in Fig. 1. First, sodium alginate was dissolved in the deionized water to form a solution, which was then decomposed at 70 °C for 48 h in order to reduce the solution viscosity. Afterward alumina nanopowder, dispersant, chelator, and calcium phosphate were added to the solution. To break down the agglomerates, the mixture was ball milled for 24 h. Degassing was subsequently carried out for 10 min in a rotary evaporator under vacuum. After adding hexandioic acid into the slurry by mechanical stirring, the resulting slurry was finally poured into a nonporous mould. The gelled wet green body was demoulded after 6–8 h and dried at room temperature for 36 h.

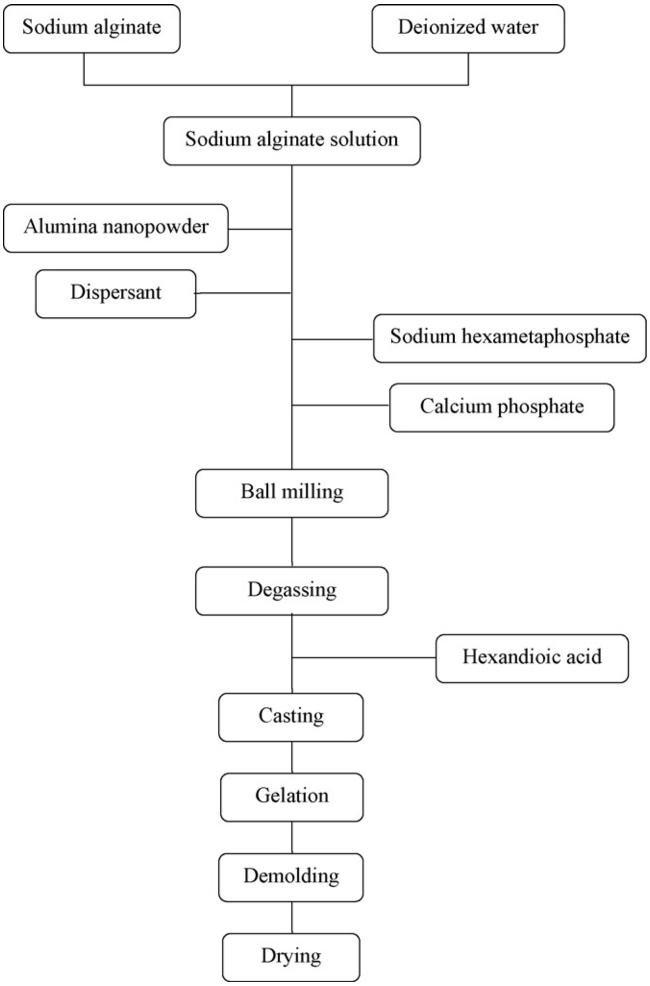

Fig. 1. Flow chart of the gelcasting process.

After drying, binder burnout and sintering were accomplished at 600 °C for 1 h with a heating rate of 1 °C/min, and at 1500 °C for 3 h with a heating rate of 2 °C/min, respectively.

2.3. Measurements

Powder morphology and microstructure of sintered bodies were studied by scanning electron microscope (SEM, XL30, Philips Co.). Phase analyses of the calcined nanopowder and sintered specimen were achieved by X-ray diffraction (Cu Kα, XPERT PW3050). The crystallite size of the synthesized powder was determined from the X-ray line broadening using Sherrer's equation:

$$B = \frac{0.9\lambda}{t\cos\theta} \qquad (1)$$

where B is the crystallite size (nm), λ the wavelength of X-ray radiation (1.54056 Å), θ the Bragg's angle, and t is the full width at half maximum (FWHM). Before calculating the crystallite size, line broadening due to the equipment was subtract from the peak width using the following formula:

$$B^2 = B^2_{\mathrm{meas}} - B^2_{\mathrm{equip}} \qquad (2)$$

Binder burnout behavior of the green bodies was determined by thermogravimetric (TG) and differential thermal analysis (DTA) (STA 1500) in air at the heating rate of 10 °C/min up to 700 °C.

Bulk density of the dried samples was calculated through division of mass to volume. The Archimedes's method was also applied in order to measure the bulk density of the sintered specimens.

Rheological properties of the slurries were determined by a rotational viscometer (Brookfield DV-II+ pro). The measurements were performed in the shear rate of 100 s^{-1} at a constant temperature of 25 °C.

3. Results and discussion

3.1. Gelation principle

Subsequent to adding divalent metallic salt into the sodium alginate solution, the sodium cation will be replaced by divalent cation, and then immediate irreversible gelation will take place [1]. Gelation reaction is shown in the following equation [2]:

$$2\text{Na-alginate} + Ca^{2+} \leftrightarrow \text{Ca-alginate} + 2Na^{+} \qquad (3)$$

Hence, the most important thing when applying sodium alginate in the gelcasting process is to control the gelation behavior by means of the chelator and initiator. In the present work, the reaction was controlled by a chelator ($(NaPO_3)_6$) and an initiator ($C_6H_{10}O_4$). It is believed that chelator and calcium react with each other and form a three-dimensional network structure which results in the stabilization of the slurry. This reaction is shown in the following equation:

$$6PO_3{}^{-} + 3Ca^{2+} \leftrightarrow Ca_3(PO_3)_6 \qquad (4)$$

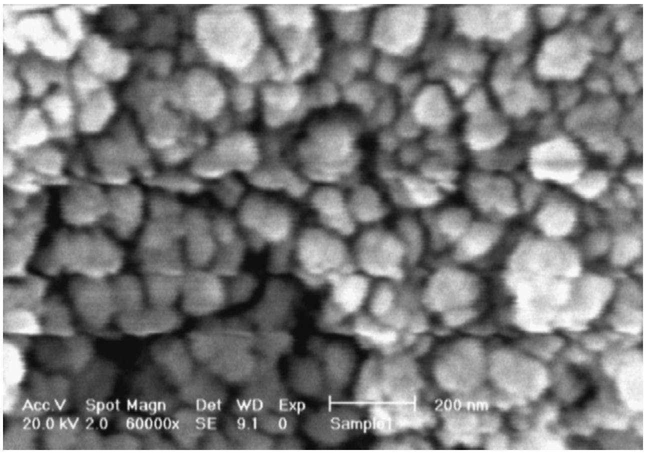

Fig. 2. SEM micrograph of alumina nanopowder calcined at 900 °C for 1 h and ball milled for 48 h.

After $C_6H_{10}O_4$ is added to the ceramic suspensions, the complex will decompose and calcium ions are released slowly (as shown in Eq. (5)), thus leading to gelation.

$$Ca_3(PO_3)_6 + 3C_6H_{10}O_4 \leftrightarrow 6HPO_3 + 3Ca^{2+} + 3C_6H_8O_4{}^{2-} \quad (5)$$

The above gelation process controlled by chelator is also used in the food industry to fabricate jelly, bean jelly, ice cream, etc. [4].

3.2. Rheological behavior of suspensions

As shown in Fig. 2, size of the particles in the synthesized alumina powder is less than 50 nm. The XRD pattern (Fig. 3) shows the resultant alumina powder to exist in the θ phase structure and therefore has a density of ~3.60 g/cm^3 [9]. The broadening of peaks in the XRD pattern confirmed the average crystallite size of the calcined powders to be in the range of 25–110 nm.

Suspensions were prepared with 16.8 vol.% solid loading (15 vol.% alumina nanopowder and 1.8 vol.% calcium phosphate) and 1 wt.% sodium alginate (based on water). The effect of the amount of dispersant (based on alumina powder) on the viscosity of the suspensions is shown in Fig. 4. The viscosity of suspensions has been found to decreases with increasing dispersant amount, due to an enhancement in the density of electron cloud on the surface of alumina nanoparticles and static repulsive force. The minimum viscosity was obtained when 2.4 wt.% dispersant was added. Beyond this value, the viscosity of slurries increases again because the free ions increase in the solution. Thus, there exists an optimum concentration (2.4 wt.%) for the amount of dispersant. This optimum point is ~8 times higher than the optimum concentration used for micron powders (~0.3 wt.% [7]), which probably pertains to the substantially higher surface area of nanopowders.

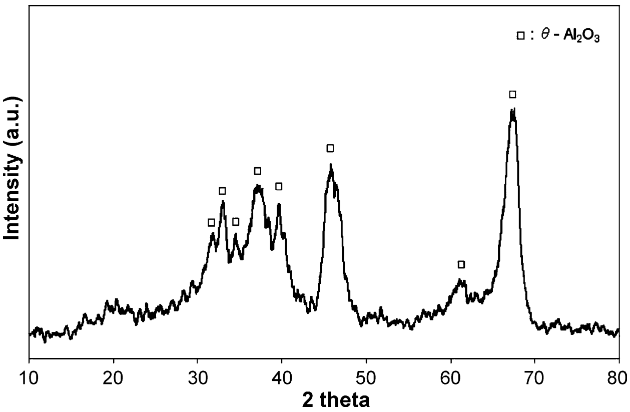

Fig. 3. XRD pattern of alumina nanopowder calcined at 900 °C for 1 h.

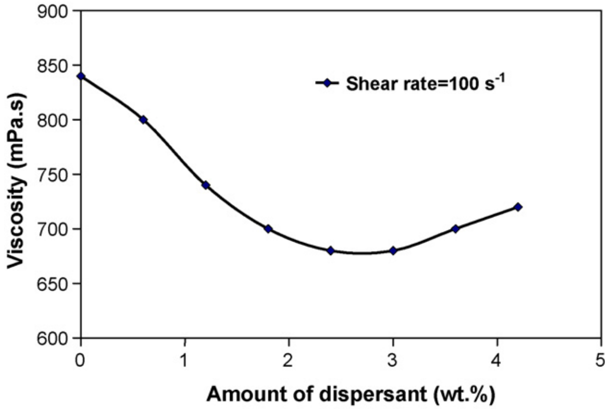

Fig. 4. Effect of amount of dispersant on the viscosity of 15 vol.% alumina suspensions.

As shown in Fig. 5, the viscosity of slurries increases rapidly with the increase of the amount of alumina nanopowder. Very high surface area of the powder justifies this fast growing of viscosity. Slurries over 15 vol.% of alumina nanopowder are not suitable for casting, because of their high viscosity and cannot fill the mould effectively. Accordingly, the properties of the obtained gel will not be satisfactory.

Based on the obtained results, slurries with 15 vol.% of alumina nanopowder, 1.8 vol.% calcium phosphate, and 2.4 wt.% dispersant were prepared. Increasing the amount of chelator (sodium hexa metaphosphate) and decreasing the quantity of initiator (hexandioic acid) would lead to an enhancement in the gelation time of the slurries [2]. Table 1

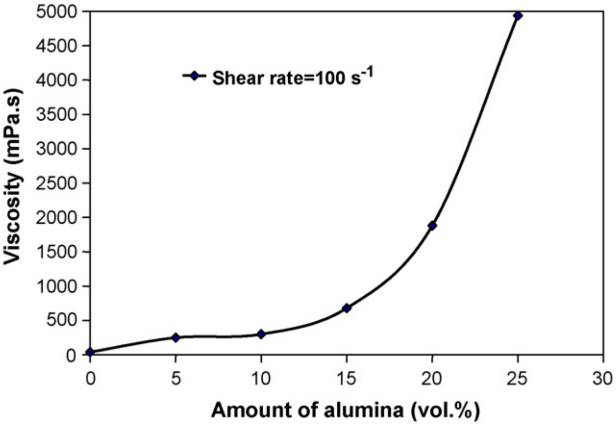

Fig. 5. Effect of amount of alumina nanopowder on the viscosity of suspensions.

Table 1
Composition of suspensions used for preparation of green bodies.

Na-Alg (ml)[a]	20
Al_2O_3 (g)	11.94
$Ca_3(PO_4)_2$ (g)	1.132
$(NaPO_3)_6$ (μl)[b]	900
$(NH_4)_3C_6H_5O_7$ (g)	0.288
$C_6H_{10}O_4$ (g)	0.564
Gelation time (min)	39

[a] The concentration of Na-Alg is 1 wt.%.
[b] The concentration of $(NaPO_3)_6$ is 20 wt.%.

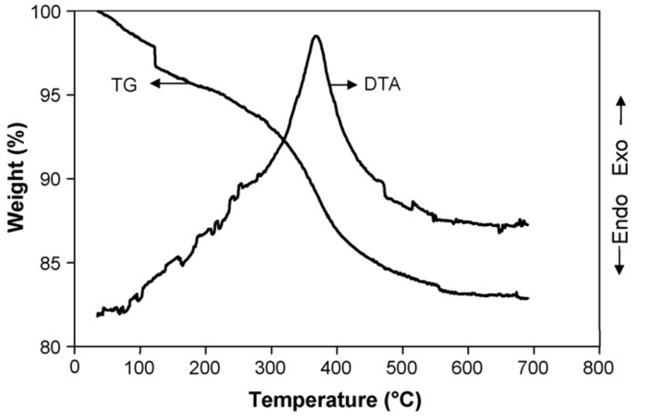

Fig. 6. TG/DTA plot for the green bodies in air.

shows the composition of the prepared slurry used to prepare green bodies. In this table, the gelation time means the duration between adding the acid and occurrence of gelation. Since the gelation is an exothermic reaction, checking the temperature of the solution will provide us with the information about the progress of the gelation. The demoulded bodies had precise size and very smooth surfaces.

3.3. *Binder burnout and sintering of green bodies*

Great shrinkage (~21%) resulted during drying of the wet gels because of the low amount of solid loading. The bulk density of the dried body is about 32% of the theoretical density.

TG/DTA analysis during binder burnout (Fig. 6) demonstrates that there is ~4% weight reduction at 130 °C which results from vaporization of the residual water. Most of other additives burnt at 280–450 °C. By raising the temperature from 25 °C to 600 °C, ~17% weight loss was observed, which could cause cracking in the green body during binder burnout. Therefore, dried bodies were heated up to 600 °C at a heating rate of 1 °C/min in order to prevent cracking.

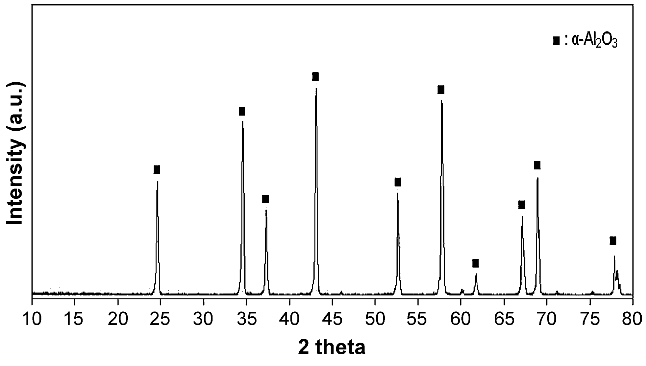

Fig. 7. XRD pattern of green body sintered at 1500 °C for 3 h.

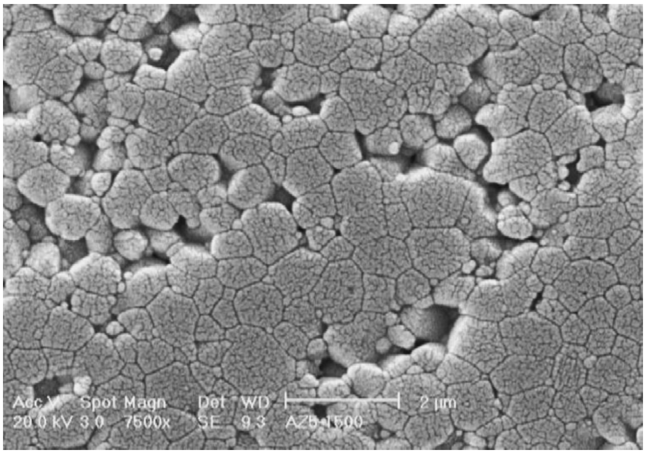

Fig. 8. SEM micrograph of green body sintered at 1500 °C for 3 h.

As shown in Fig. 7 only α-alumina was detected in the sintered specimen. No other phases containing Na, Ca and P were detected due to their very low content.

Fig. 8 presents a SEM micrograph of Al_2O_3 ceramic. It should be noted that, no huge grain growth exists. The sintered body has a bulk density of ~89% T.D. and shows uniform porous microstructure.

4. Conclusions

Sodium alginate was applied for in situ forming of Al_2O_3 green bodies from nanopowders. Slurries with 15 vol.% alumina and 1.8 vol.% calcium phosphate dispersed by 1 wt.% sodium alginate solution, were prepared for the gelcasting process. The obtained results can be summarized as follows:

(1) Sodium alginate was successfully used in the gelcasting process of alumina nanopowder.
(2) Reological behavior of slurries containing nanopowder is strongly affected by nanopowder volume fraction.
(3) The required amount of dispersant for alumina nanopowders is about eight times than that for micron powders.
(4) Producing ceramic parts composed of homogenous and nano-grained microstructure, and without huge grain growth, was feasible.

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