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Fabrication of alumina green body through gelcasting process using alginate

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Abstract

In the present work, we studied the addition of sodium alginate, a natural innoxious polymer, to coagulate alumina slurry in the fabrication of an Al_2O_3 green body. Calcium iodate was added into the alumina suspension that was dispersed in a sodium alginate solution. The slurry was stable at room temperature but it solidified with increasing temperature. A slurry of 50 vol.% alumina ceramic powder, 1 wt.% calcium iodate and 1 wt.% sodium alginate solidified after being heated at 60 °C for 1 h. In addition to this process, a chelator was used to control the gelation behavior. Associated with the effect of the chelator, the consolidation reaction rate was delayed to longer than 30 min. The gelling properties of the sodium alginate solution and the resultant alumina slurry were analyzed. The rheological behavior of the slurry was examined. Appropriate forming processes were determined. Near-net-shaped green bodies were produced. The resultant green body has uniform structure and smooth surface, and the bonding strength is as high as 8.0 MPa.

Keywords: Casting; Ceramics; Sodium alginate; Suspensions; Polymer; Al_2O_3

1. Introduction

The gelcasting method was first introduced to the ceramic forming process by Prof. Omatete and his research group [1]. In the process, ceramic powders are dispersed into a water-based monomer solution. After a catalyst and initiator are added, the slurry solidifies. This forming process has two outstanding merits: (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 [1,2]. However, its inevitable shortcoming, the commonly used monomer acrylamide that exhibits neural toxicity [3], limits its application. More and more researchers studied nontoxic or low toxicity polymers in the process. Agar has been used in fabrication of alumina ceramics [4]. Gelatine has been used in the gelcasting process [5]. In the present work, a natural innoxious polymer-sodium alginate was used to coagulate the alumina ceramic suspension.

Alginate, a natural innoxious polymer, was frequently applied in the injection process for ceramics [6]. In recent reports, it was used in the fabrication of silicon nitride beads [7]. In the present research, it is utilized in the in situ forming process of ceramics by adjusting its gelling behavior.

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2. Experimental procedures

2.1. Raw materials

Alumina powders were produced by Henan Xinyuan Aluminum Industry in China (mean particle size, 2.9 μm; specific surface area, 0.434 m^2/g). Sodium alginate (NaAlg), calcium iodate ($Ca(IO_3)_2$), calcium phosphate ($Ca_3(PO_4)_2$), hexandioic acid ($C_6H_{10}O_4$), sodium hexa metaphosphate ($(NaPO_3)_6$) and ammonium citrate tribasic ($(NH_4)_3C_6H_5O_7$—the dispersant) were supplied by Beijing Chemical reagents company as fine powders.

2.2. Procedures

The gelcasting flow chart of the system containing calcium iodate is presented in Fig. 1. At first, sodium alginate was dissolved in deionized water. After alumina ceramic powder and dispersant were added in, the mixture was rolling milled with zirconia balls (the diameter of the zirconia balls is from 5 to 8 mm, the

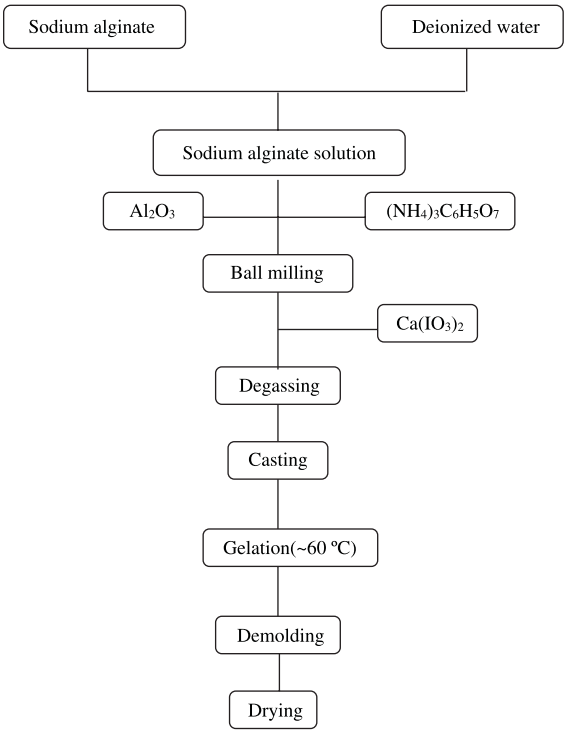

Fig. 1. Flow chart of the forming process with calcium iodate.

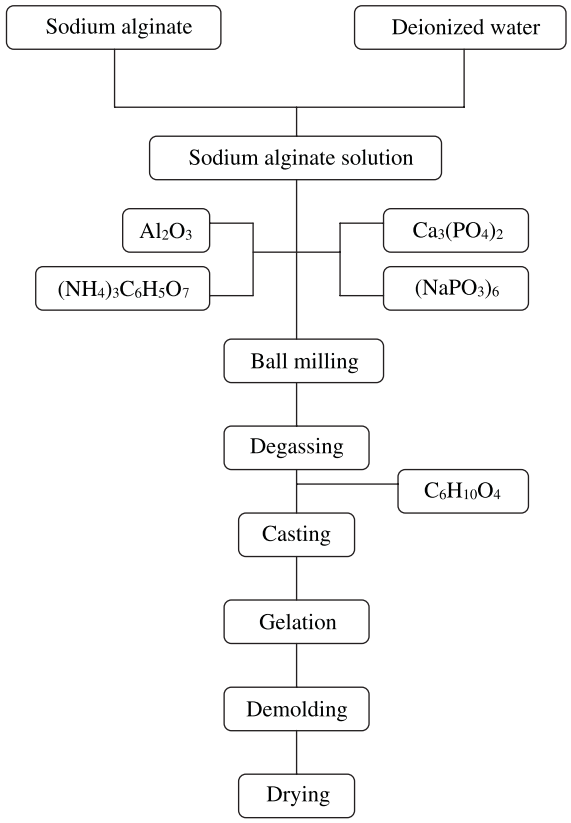

Fig. 2. Flow chart of the forming process with chelator.

powder to zirconia balls ration is 1:1) for 12 h to break down the agglomerates. After adding calcium and degassing, the resulting slurry was poured into a nonporous mould and heated to 60 °C. The gelled wet green body was removed from the mould after casting for about 6 h.

Fig. 2 describes the flow chart of the system containing chelator. Calcium salt and chelator were introduced before ball milling. After the slurry had been milled and degassed, hexandioic acid was added under mechanical stirring. The resulting slurry was cast into the mould and gelled at room temperature.

2.3. Measurements

The apparent viscosity was measured by a rotating viscometer (model NXS-11) of Chengdu Instruments Plant (China). The gelation time t was determined by checking the suddenly increasing turning point of the slurry temperature. Flexural strength of green bodies,

which were cut to a size of $3 \times 4 \times 36$ mm, was determined by a three-point flexure test with span of 30 mm at 0.5 mm/min loading rate. The microstructure of the green body was observed by scanning electron microscope (SEM, Hitachi S-450).

3. Results and discussion

3.1. Effect of calcium iodate added on the gelation of alginate solution

Sodium alginate can be dissolved in water at room temperature by mechanically stirring, and the irreversible gelation starts as soon as sufficient divalent metal ions are present. When adding a divalent metallic salt solution into the sodium alginate solution, the gelation reaction takes place immediately and unevenly. Therefore, control of its gelation behavior and consolidation of the ceramic slurry in the demanded time period is required when applying it to the gelcasting process of ceramics.

The solubility of calcium iodate increases with the temperature. Its solubility is only 0.17 wt.% at room temperature, but increases to 1.38 wt.% at 60 °C. Based on this property, 1 wt.% calcium iodate was dispersed in a 3 wt.% alginate solution, and then the mixture was heated in a 60 °C water bath (all concentrations appeared in this paper are based on water). Fig. 3 presents the viscosity curve of the

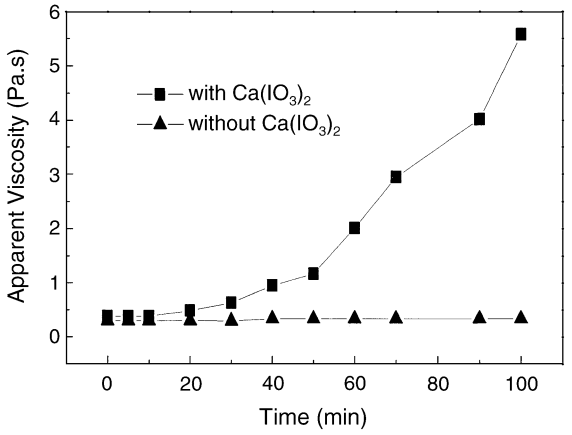

Fig. 3. Time-dependent viscosity of 3 wt.% sodium alginate solution with or without 1 wt.% calcium iodate after it had been placed in a 60 °C water bath (at the shear rate of 50.19 s^{-1}).

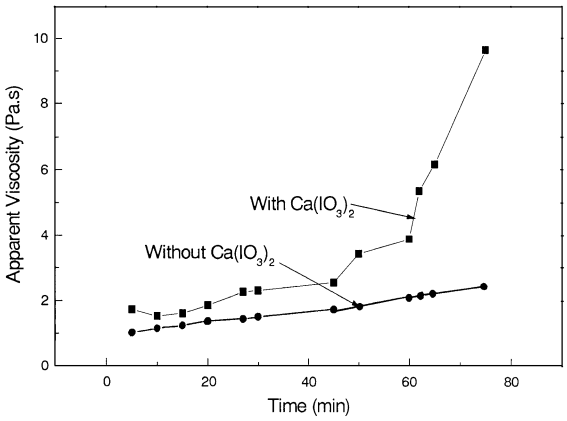

Fig. 4. Increase of viscosity of 50 vol.% alumina slurry with or without 1 wt.% calcium iodate plotted against heating time (at the shear rate of 50.19 s^{-1}).

suspension. Initially, the viscosity of the suspension with calcium iodate increases very slowly. After being heated for more than 40 min, the apparent viscosity increases significantly until the gel is formed. On the other hand, the viscosity of the suspension without calcium iodate does not change during the heating process. It is believed that the released calcium ions bond the alginate molecular chains after the mixture is heated at 60 °C, and a three-dimensional network structure is formed because of the attraction among the molecular chains.

Based on this knowledge, the gelling properties of the slurry with 50 vol.% alumina in the presence of 1 wt.% sodium alginate and 1 wt.% calcium iodate were investigated. As shown in Fig. 4, when the slurry is heated in a 60 °C water bath for more than 40 min, the apparent viscosity of the slurry increases significantly. When the slurry was heated for more than 1 h, a wet green body is gelled soon. At the same time, the viscosity of the slurry without calcium iodate increases only slightly, which might be caused by water evaporation. These results suggest that the alumina slurry with sodium alginate is gelled by the addition of calcium iodate and the casting process can be controlled by the final temperature.

Since the volume of calcium iodate is small, as shown in the flow chart (Fig. 1), it was added into the slurry after ball milling and dispersed by stirring. The viscosity of the slurry would increase, while calcium iodate was added before the ball milling process. In

this case, calcium ions are released under the action of mechanical stress, which introduces the gelation of alginate and then increases the viscosity of the slurry [6]. As it is obvious from Fig. 5, the microstructure of the produced alumina green body is compact and homogeneous.

3.2. Role of the chelator to control the gelation of alginate

The mechanical strength of the resultant ceramic green body is determined by the bonded strength of the alginate molecular chains, which are attracted by the calcium ions. Since the solubility of calcium iodate is not so high even at 60 °C, the mechanical strength is low and the green body can be broken by hand easily. In view of this aspect, another method, using a chelator to control the gelation behavior, was developed.

When adding calcium salt and a chelator for calcium into the sodium alginate solution simultaneously, the solution keeps stable due to the chelation between the calcium ions and chelator. After addition of hexandioic acid, the combination is disbanded and released calcium ions initiate the gelation reaction of alginate.

In the food industry, the gelation process controlled by chelator is commonly used to fabricate jelly, bean jelly, ice cream, etc. The widely used calcium salt is calcium phosphate ($Ca_3(PO_4)_2$), and sodium hexa metaphosphate ($(NaPO_3)_6$) is used as chelator [6]. In the present work, these materials have been used in the process containing chelator.

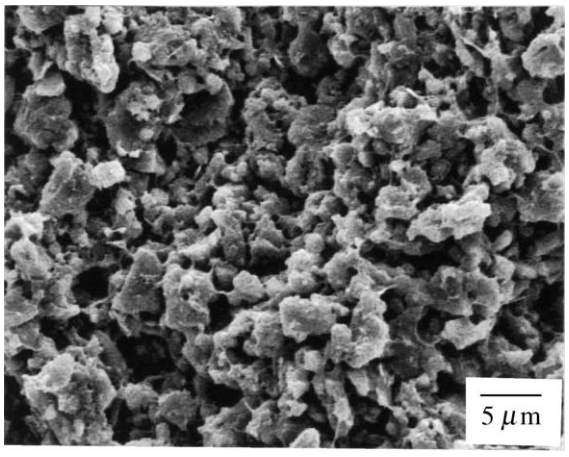

Fig. 5. SEM micrograph of alumina ceramic green parts made by the forming process with calcium iodate.

Table 1
The influence of chelator on the gelation of sodium alginate solution

	Sample			
	1	2	3	4
NaAlg (ml)	20	20	20	20
$C_6H_{10}O_4$ (g)	0.15	0.15	0.15	0.15
$Ca_3(PO_4)_2$ (g)	0.3	0.3	0.3	0.3
$(NaPO_3)_6$ (μl)	120	240	440	500
t (min)	<1	3	18	>30

C_{NaAlg} = 1 wt.%; $C_{(NaPO_3)_6}$ = 20 wt.%.

Table 1 shows the influence of the chelator on the gelation behavior of the alginate solution. The gelation time t of the gelation means the time between acid addition and the gelation. Because the gelation is an exothermic reaction, the increase of the slurry temperature indicates the gelation reaction.

As shown in Table 1, the gelation reaction is delayed to more than 30 min with increasing chelator. The reason is that the free calcium ions in the solution were limited due to the chelation, which results in a delay of the gelation reaction between alginate and calcium ions.

On the basis of this data, the chelator has been used in the forming process of alumina ceramics. Table 2 indicates the influence of the chelator on the gelling process of the slurry. By adding the chelator, the gelling behavior of the slurry can be easily adjusted. In order to improve the mechanical strength of the green body, the amount of added calcium salt has been increased to about 10 wt.% (samples 6–8). The

Table 2
The influence of chelator on the gelation of alumina slurry

	Sample			
	5	6	7	8
NaAlg (ml)	20	20	20	20
$C_6H_{10}O_4$ (g)	0.15	0.15	0.6	0.6
$Ca_3(PO_4)_2$ (g)	0.3	2.3	2.3	2.3
$(NH_4)_3C_6H_5O_7$ (g)	0.2	0.2	0.2	0.2
Al_2O_3 (g)	72	72	72	72
$(NaPO_3)_6$ (μl)	440	440	600	1000
t (min)	15	5	10	28
Flexural strength (MPa)	<2	7.8 ± 2.5	8.1 ± 2.7	8.0 ± 2.4

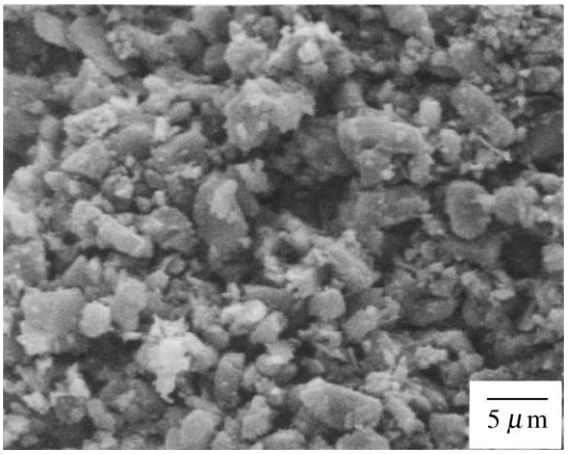

Fig. 6. SEM micrograph of alumina ceramic green body made by forming process with chelator.

strengths of samples 6, 7 and 8 are almost the same, which are much higher than that of the sample 5. The reason is that the strength is determined by the cross-linking of polymer chains, which is originated from the action of calcium ions between two chains [6]. On considering that the mechanical properties of the final ceramic are badly affected by too many impurities, much higher calcium salt concentration should be avoided. Of course, the increase of the amount of calcium salt means that more chelator is required in order to keep the slurry stable. In turn, a larger amount of hexandioic acid must be added to set free the calcium ions for coagulation. The flow chart is presented in Fig. 2.

It can be seen in Fig. 6 that the resulting green body has a homogenous and compact microstructure without apparent agglomerates or pores. After the drying process, the green body has a linear shrinkage of 2–3%. The mechanical strength of the green body (the same composition as sample 8) is 8.0 ± 2.4 MPa.

After the green body with agglutinants (CaO: 1.8 wt.%, SiO_2: 2.2 wt.%; CaO is introduced by $Ca_3(PO_4)_2$ which content is the same as sample 8) is sintered at 1550 °C for 2 h, the relative density of final ceramic is about 98.7% (determined by Archimedes method). No special binder removal treatment had been carried out since the content of the NaAlg is lower than 0.3 wt.% of the green body. The detailed information of the sintered ceramics fabricated by the present method is given elsewhere [8].

4. Conclusions

(1) Sodium alginate can be successfully utilized in the gelcasting process for alumina ceramics by controlling its gelation behavior.
(2) After adding calcium iodate into the sodium alginate solution, the gelation behavior can be controlled by adjusting the temperature. The alumina ceramic green body can be fabricated by applying the proposed method.
(3) The gelation behavior of alginate can be easily controlled by using chelator and hexandioic acid. The alumina ceramic green body fabricated by the present process has precise size and smooth surface. SEM shows that the microstructure of the green body is homogenous and compact without apparent agglomerate or pores.
(4) The linear drying shrinkage of the green body is 2–3%; the mechanical strength of the dry body is 8.0 ± 2.4 MPa.

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