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Effect of atmosphere type on gelcasting behavior of Al_2O_3 and evaluation of green strength

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Abstract

Gelcasting of Al_2O_3 was performed in air, vacuum (38 torr), and N_2 to find the influence of atmosphere type. The strength of gelcast green bodies was determined by a flexural test and compared with those of dry-pressed and slip-cast bodies. It was found that the atmosphere types containing oxygen, such as air and vacuum (38 torr), was improper for gelcasting since the formation of strong binder networks by the in-situ polymerization of monomers failed in the surface regions, resulting in an exfoliation problem of the formed bodies. Such a problem could be avoided with N_2 atmosphere. The flexural strength of the gelcast green bodies was determined to be 30.8 MPa, which was about 14 and 22 times higher than those of dry-pressed and slip-cast bodies, respectively. This high green strength was attributed to the well-developed binder networks by the polymerization of monomers, as confirmed by SEM.

Keywords: A. Shaping; C. Strength; D. Al_2O_3; Gelcasting

1. Introduction

Gelcasting is a novel forming method for making complex-shaped ceramic bodies [1–4]. In this process, a ceramic powder slurry is prepared with a water-based monomer solution and then polymerized in situ after casting into a mold, producing a macromolecular network to hold the ceramic particles together. Distinct advantages of the gelcasting over the conventional ceramic forming processes such as dry pressing, slip casting, and injection molding are near-net-shape forming, high green density, low levels of organic additives, and machinability in the green state due to a high strength [1,2].

Both nonaqueous and aqueous solvents can be used for gelcasting. But, aqueous system is preferred because the use of water as the solvent has many advantages, e.g. less departure from traditional ceramic processing and no environmental problems for disposal. In the aqueous gelcasting, acrylamide (AM) and methylenebisacrylamide (MBAM) are commonly used to make monomer solutions [1–3]. Recently some monomer systems other than acrylamide have been investigated, which are low in toxicity [4]. According to the previous studies [1,2], the composition of monomer solution, the amounts of initiator and catalyst additions, and the humidity of drying atmosphere are important processing parameters to be controlled for optimum gelcasting.

The polymerization of AM and MBAM is a free-radical reaction process in which polymerization can be inhibited by atmospheric oxygen [5,6]. Hence, the atmosphere type for gelcasting must be another important processing parameter to be considered. No specific results, however, have been reported about the effects of atmosphere type on the gelcasting behavior of ceramics. Although one of the important features of gelcasting is known to be high green strength, quantitative evaluation studies are very rare in the literature. The work by Nunn et al. [3] seems to be the only one in which the tensile strength of dried gelcast green bodies of Al_2O_3 was determined by a diametral compression test with disk-shape samples.

In the present work, gelcasting of Al_2O_3 was performed under three different atmospheres, i.e. air, vacuum (38 torr), and N_2 in order to find the influence of atmosphere type. In addition, the green strength of

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gelcast bodies was evaluated using a flexural test, which is the common test method for ceramics. This was compared with the flexural strength of green bodies prepared by conventional dry pressing and slip casting.

2. Experimental procedure

An α-Al_2O_3 powder with a mean particle size of 0.5 μm (99.8%, AES-11, Sumitomo Chemical Co., Japan) was used. The monomers used are acrylamide (AM), $C_2H_3CONH_2$, and methylenebisacrylamide (MBAM), $(C_2H_3CONH)_2CH_2$ (Sigma Chemical Co., St. Louis, MO, USA). Ammonium persulfate, $(NH_4)_2S_2O_8$ and N,N,N′,N′-tetramethylethylenediamine (TEMED), $C_6H_{16}N_2$ (Sigma Chemical Co., St. Louis, MO, USA) were used as an initiator and a catalyst, respectively, for the free-radical polymerization reaction of monomers.

The monomers were dissolved in deionized water to make solution with a composition of 14 wt% AM, 0.6 wt% MBAM, and 85.4 wt% water, which is one of the representative compositions of monomer solution suggested in the previous work [2]. Gelcasting slurries were prepared by ball-milling the alumina powder in the monomer solution. Darvan C (R.T. Vanderbilt Co., Inc., Norwalk, CT, USA), 0.67 wt%, was added as a dispersant for the alumina powder. In the slurries, the solid loading was 55 vol%, and the total amount of organic monomers was about 3.4 wt% for the powder. Both the initiator, 1 wt% aqueous solution of ammonium persulfate, and the catalyst, TEMED, were added just before casting into a mold. To investigate the effect of atmosphere type during gelation, the slurries were cast in plastic-cup molds at room temperature in air, vacuum, and N_2. The casting under vacuum or N_2 was performed in a chamber filled with N_2 or evacuated to 38 torr (0.05 atm) with a motor-driven aspirator, respectively. After gelation, the disk-shaped samples (50 mm diameter and about 7 mm thickness) were demolded and dried in lab atmosphere (i.e. air, 17–22°C, and 32–40% relative humidity) without a special care of the humidity. Drying and gelation behavior of the samples was examined by observing the appearances and microstructures visually and by scanning electron microscopy (SEM). In the case of samples for flexural tests of green strength, gelcasting was performed in a steel mold with rectangular cavities in N_2. The bar-shaped samples obtained after demolding were dried in the lab atmosphere, and machined and finished to the size of about $8\times5\times35$ mm.

For comparison with the gelcast samples on the green-body strength, dry-pressed and slip-cast samples with a bar shape ($8\times5\times35$ mm in size) were prepared. The powder for dry pressing was prepared by wet ball milling the alumina powder with a binder and a lubricant. Polyvinyl alcohol (PVA, M.W. 9000–10000, Aldrich Chemical Co., Milwaukee, WI, USA) and stearic acid emulsion (Nopcocera LU-6418, Korea Sanopco Co., Seoul, Korea) were used as the binder and lubricant with additions of 4 and 1 wt% for the powder, respectively. The PVA addition, 4 wt%, was chosen to ensure a sufficient binder amount compared with the amount of monomer binders in the gelcast samples, 3.4 wt%. The ball-milled slurry was dried and the resulting powder was crushed and then sieved through a 100 mesh screen. Bar samples for a flexural test were formed by uniaxially pressing the sieved powder at 36 MPa, followed by isostatic pressing at 200 MPa. The slip casting slurry was prepared also by ball milling the alumina powder in distilled water with the dispersant, 0.67 wt% Darvan C, and the binder, 0.5 wt% carboxymethyl cellulose (CMC, viscosity 10–55 cps for 4% aqueous solution, Aldrich Chemical Co., Milwaukee, WI, USA). The use of 0.5 wt% CMC is a common recipe for alumina slurries for slip casting [7], since a more addition generally makes the slurry fluidity inadequate for slip casting. The solid loading in the slurry was about 38 vol% (or 71 wt%). The slip casting slurry was cast in a plaster of paris mold with rectangular cavities. The bar-shaped samples obtained after demolding was completely dried in an oven at 50°C.

SEM works, to find any difference in the distribution and state of the polymerized binder, were performed on the fracture surfaces of gelcast samples prepared under the different atmospheres. The flexural tests for measuring the green strengths of gelcast, dry-pressed, and slip-cast samples were performed in three-point mode with the span 20 mm on a universal testing machine. At least five samples were tested to obtain the average strength value for each kind. The green densities of the flexural test samples were measured by the Archimedes method using the pieces of the tested samples after coating with a paraffin wax.

3. Results and discussion

Fig. 1 shows the appearances of gelcast samples after drying, prepared under air, vacuum, and N_2. The

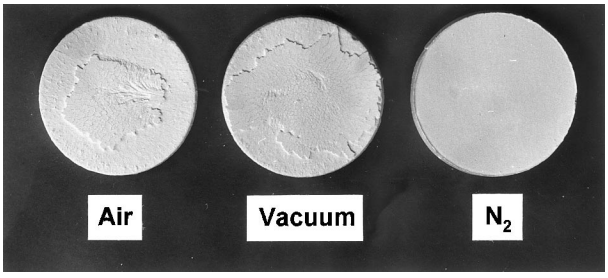

Fig. 1. Photographs comparing the appearances of the samples gelcast in air, vacuum, and N_2 after drying. Note the exfoliation of the surfaces for the air and vacuum conditions.

samples gelcast in air and vacuum exhibited exfoliation of the surfaces exposed to the atmospheres during gelcasting. Although the interior of samples was rigid, the surface regions exfoliated were fragile, implying a failure in the formation of a strong binder network by the in-situ polymerization of monomers here. In contrast, the sample gelcast in N_2 exhibited no evidence of exfoliation with good rigidity of the overall body. It is also notable that no cracking and warping occurred in all the three kinds of samples, although they were just dried in the lab atmosphere without a special control of humidity. This is different from the suggestion by the previous works [2,3] that, to avoid warping and cracking due to rapid drying, gelcast bodies need to be dried in a controlled-humidity chamber at room temperature, with as high as 92% or above relative humidity until complete shrinkage.

In order to find any difference in the presence of binders between the surface region exfoliated and the interior of samples gelcast in air and vacuum, the fracture surfaces of these regions were observed by SEM as shown in Fig. 2. In the case of the exfoliated region, Fig. 2(a), there was no presence of binder networks, whereas in the case of the interior region, Fig. 2(b), binder networks holding the alumina particles together were evidently observed. Therefore, it is assured that in the surface regions exfoliated, the atmospheric oxygen attacked to a certain depth and inhibited the polymerization of AM and MBAM monomers, a free-radical reaction process negatively affected by the presence of oxygen [5,6]. The vacuum level (38 torr), obtained by an aspirator in this work, was not so high that there was a good amount of oxygen. The fracture surface of the sample gelcast in N_2 showed the same feature as in Fig. 2(b), i.e. well-developed binder networks, as predicted from the rigidity of overall body. From these results, it is evident that the use of an oxygen-free atmosphere such as N_2 is necessary for successful gelcasting without the exfoliation problem of the formed bodies.

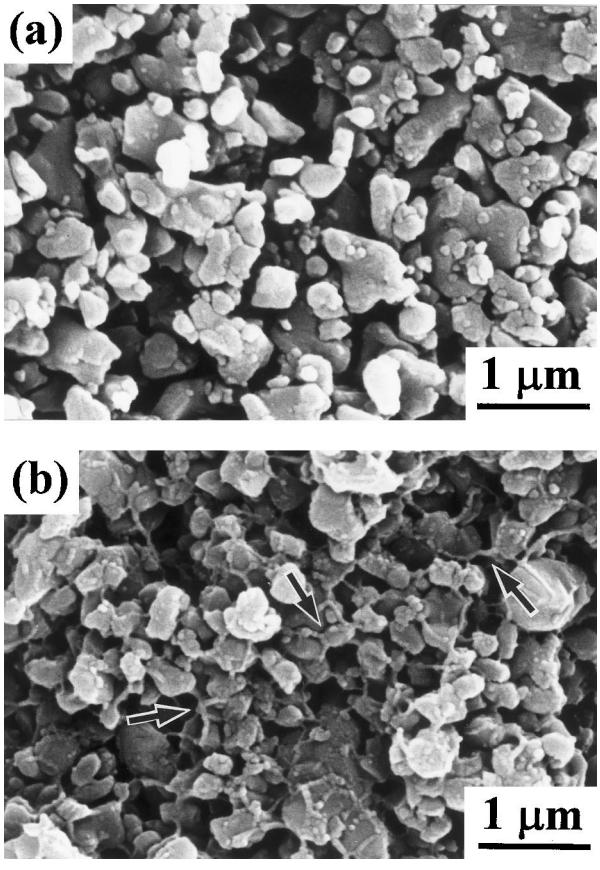

Fig. 2. Typical scanning electron micrographs of the fracture surfaces of the samples gelcast in air and vacuum: (a) the surface region exfoliated, (b) the interior. Note the binder networks holding the alumina particles together in (b), as indicated by the arrows.

Table 1 shows the green densities of gelcast, dry-pressed, and slip-cast samples with the results of flexural tests to measure the green strength. The gelcast and dry-pressed samples had nearly the same densities as high as about 59% theoretical density (TD) of alumina. On the other hand, the slip-cast sample had slightly a lower density, 54% TD. The green strength of the gelcast sample was found to be 30.8 MPa, which is incredibly higher than those of dry-pressed and slip-cast samples, 2.1 and 1.4 MPa, respectively. As mentioned above, there was almost no difference in the green density between the gelcast and dry-pressed samples. Furthermore, the binder content was rather less in the gelcast sample, as shown in Table 1. Considering these facts, it is apparent that the high green strength of the gelcast sample entirely results from the well-developed binder networks by the polymerization of the monomers, as confirmed in Fig. 2(b). Previously [3], the tensile strength of alumina green bodies, gelcast with nearly the same conditions as in the present work, was determined to be 2.93 MPa by a diametral compression test. Compared with this, the gelcast sample in the present work showed a much greater strength, although the test method was different.

Table 1
Binder content, and green strengths of gelcast, dry-pressed, and slip-cast samples

Sample	Binder	Green density		Green strength (MPa)
		(g/cm^3)	(% TD[a])	
Gelcast	3.4% AM/MBAM	2.33	58.5	30.8
Dry-pressed	4 wt% PVA & 1 wt% LU-6418	2.36	59.3	2.1
Slip-cast	0.5 wt% CMC	2.16	54.3	1.4

[a] Theoretical density of alumina (3.98 g/cm^3).

4. Conclusions

The atmosphere types containing oxygen, such as air and a low vacuum (38 torr), were found to be improper for gelcasting since the formation of strong binder networks by the in-situ polymerization of monomers failed in the surface regions, resulting in an exfoliation problem of the formed bodies. Such a problem could be avoided by the use of N_2 atmosphere. The flexural strength of the gelcast green bodies was determined to be 30.8 MPa, which was about 14 and 22 times higher than those of dry-pressed and slip-cast bodies, respectively. This high green strength was attributed to the well-developed binder networks by the polymerization of monomers, as confirmed by SEM examination.

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