Direct Coagulation Casting of Alumina Slurries Stabilized through Zirconium Acetate Using an Enzyme-Catalyzed Reaction

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A direct coagulation casting (DCC) method to establish near-net-shape was investigated. DCC was performed using alumina slurry with different concentrations of zirconium acetate (Zr-Ac), which was used as the dispersant for preparation of the alumina slurry over the weak acidic range. Green bodies were fabricated from these slurries by the DCC method using the enzyme-catalyzed urea-urease reaction for 24 h. Accurate sintered bodies could be fabricated by this DCC method, which used alumina slurries prepared with addition of Zr-Ac over the effective range. The relative densities of the sintered bodies at 1,500 °C were more than 99.3 %.
Key words: Direct coagulation casting, Urea-urease, Enzyme-catalyzed reaction, Al_2O_3 slurry, near-net-shape

1. INTRODUCTION

There have been a number of attempts to establish practical near-net-shaping techniques for use in ceramics forming[1]-[7]. Recently, direct coagulation casting[8]-[12] (DCC) methods using enzyme-catalyzed reactions have been proposed as means to establish near-net-shape. DCC methods have the following characteristics: (1) an accurate homogeneous green body is fabricated by solidifying the thickening slurry; (2) instead of using a plaster mold, various materials can be used as the mold; (3) the molds can be used repeatedly; and (4) DCC can be used to fabricate more complex ceramic products than can be prepared by slip casting.

The most important reaction[1],[2],[11] is the hydrolysis of urea, which is catalyzed enzymatically by urease:

$$(NH_2)_2CO + 2H_2O \xrightarrow{\text{urease}} 2NH_3 + H_2CO_3$$
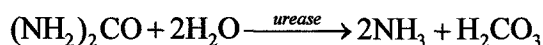
The reaction kinetics is determined by the urease activity and urea concentration, and is dependent on the temperature. The fluidity of the thickened slurry is reduced by the enzyme-catalyzed urea-urease reaction, and shifting the pH from the acidic range to pH 9 and increasing the ionic strength solidify the slurry.

The DCC method requires thickening of the slurry, while maintaining low viscosity. For the dispersion and fluidity of alumina (Al_2O_3) slurry at pH 4.3, we reported that the effective amount of zirconium acetate (Zr-Ac) was over a very wide range from 1×10^{-6} M to 1×10^{-2} M, and the Al_2O_3 slurry with 1×10^{-4} M Zr-Ac could be thickened up to 85.7 wt%, while maintaining its fluidity[12]. At pH > 4.3, the viscosity of the Al_2O_3 slurry with Zr-Ac increased, and the slurry finally coagulated. Therefore, we[11] reported the effect of hydrolysis reaction temperature and urea concentration on the solidification onset time of 84 wt% Al_2O_3 slurries with 1×10^{-4} M Zr-Ac. We showed that the slurries began to solidify in the presence of urea at concentrations over 0.02 M at 25 °C.

Generally, organic solvents can be used to completely dry the green bodies within a very short time because they are highly volatile. However, the use of large amounts of organic solvent has serious environment impact. Therefore, to reduce environmental impact, it is important to develop processes that use water as the solvent.

The present study was performed to evaluate the effects of the amount of Zr-Ac on the DCC method using the enzyme-catalyzed urea-urease reaction and to determine the effect on the onset time of solidification of Al_2O_3 slurries. The green and sintered bodies were evaluated by measuring their densities and degrees of shrinkage and by microstructural observation.

2. Experimental Procedures

2-1 Materials

In this study, commercial-grade Al_2O_3 powder (AKP-30, Sumitomo Chemical Co., Tokyo, Japan) was used. The average particle size, specific surface area, and density of the Al_2O_3 powder were 0.33 μm, 6.8 m^2 g^{-1}, and 3.96 g cm^{-3}, respectively. Water used was from a Milli-Q system (Millipore Co., Bedford, MA). Zr-Ac (Aldrich Chemical Co., Madison, WI) was used as the dispersant for the slurries. HNO_3 was added to adjust the pH of the slurries. Urea (purity 99.0 %, Nacalai Tesque, Inc., Kyoto, Japan) and highly pure jack bean urease (1.32×10^5 U g^{-1}, Toyobo Co., Inc., Osaka, Japan) were used for the enzyme-catalyzed reaction to consolidate the slurry. One unit (U) of urease activity was defined as that which liberated one micromole of ammonia per minute at 25 °C in phosphate buffer at pH 7.3.

2-2 Preparation of slurry and compact

High Al_2O_3 loading slurries (84 wt%) were prepared by ball milling with zirconia balls for 24 h at room temperature. The slurries containing 3.0×10^{-2} M urea were adjusted to pH 4.3. To investigate its dispersing effect, Zr-Ac was added to the slurries at concentrations of 1×10^{-5}, 1×10^{-4}, 1×10^{-3}, and 1×10^{-1} M. After ball milling and degassing, urease stock solution (4×10^5 U L^{-1}) was added to 100 mL of the Al_2O_3 slurry, and then the slurries were mixed using a planetary mixer

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(MS-SNB 350N, Matsuo Industry, Osaka, Japan). Mixing time was 150 s and revolution and rotation rates were 1,058 rpm. The prepared slurries were cast into nonporous polypropylene molds. The slurries were solidified at 27 °C and R.H. of 98 % in a climatic test chamber (Sanyo Electric Co., Osaka, Japan) for 24 h. The green bodies were removed from the mold and dried at room temperature for 24 h. They were then calcined in air by heating at a rate of 1 °C min^{-1} to 600 °C, at which temperature they were held for 2 h. To obtain the sintered bodies, the temperature was elevated to the sintering temperature (1,400, 1,500, or 1,600 °C) at 2 °C min^{-1} and held there for 2 h in air.

2-3 Measurements

The solidification onset times of the slurries were determined by dynamic rheological measurements (oscillation techniques) using a rheometer (RS-150, Haake, Karlsruhe, Germany). The oscillatory measurements were investigated with a stress of 5 Pa and a frequency of 1 Hz for 5,000 s. The complex shear modulus (G*) measured consisted of a storage modulus component (G') and a loss modulus component (G''). In this study, the time at which G' began to increase was defined as the solidification onset time of the slurry.

The apparent density and linear shrinkage of green bodies fabricated via the DCC process were measured. The linear shrinkage of green bodies was calculated from the sizes of the molds used. Furthermore, the bulk density and linear shrinkage of sintered bodies were measured by the Archimedes method and by determining shrinkage from the green compacts, respectively. Microstructural observation was performed by scanning electron microscopy (SEM, S-4300, Hitachi High-Technologies Co., Tokyo, Japan) of polished and thermally etched surfaces of the sintered bodies fired at 1,500°C. Thermal etching was performed in air for 15 min at 1,400°C.

3. Results and discussion

3-1 Effects of the amount of urease added on the onset time of solidification of the slurry

In this study, we considered the influence of the amount of urease on solidification onset time of Al$_2$O$_3$
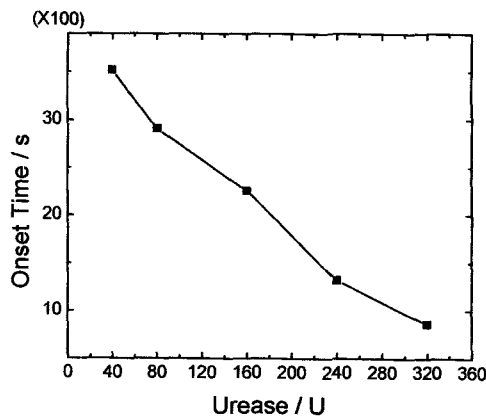

Fig. 1 Effects of the amount of urease added to 100 mL of Al$_2$O$_3$ slurry with 1×10^{-4} M Zr-Ac and 3.0×10^{-2} M urea at 25 °C on the solidification onset time of the slurry.
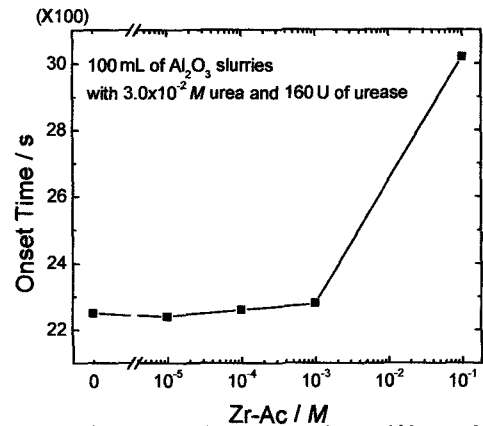

Fig. 2 Effects of Zr-Ac concentration in 100 mL of Al$_2$O$_3$ slurry with 3.0×10^{-2} M urea and 160 U urease on the solidification onset time.

slurries. Urease was added to 100 mL of Al$_2$O$_3$ slurry with 1×10^{-4} M Zr-Ac and 3.0×10^{-2} M urea at 25 °C. Figure 1 shows the relationships between the amount of urease and the solidification onset time determined by oscillatory measurements. The solidification onset time was reduced with increasing amount of urease. The slurry did not undergo consolidation when left to stand for 5,000 s after the addition of < 40 U of urease. On the other hand, when 360 U of urease was added, the Al$_2$O$_3$ slurry solidified immediately. The solidification onset time of the slurry containing 3×10^{-2} M urea could be controlled by adjusting the amount of urease added. Taking into account working time as mixing, degassing, and casting, the optimal amount of urease for DCC was 160 U, with which the slurry began to solidify after 2,300 s.

3-2 Effects of Zr-Ac concentration on the solidification onset time of the slurry

The influence of various concentrations of Zr-Ac on the solidification onset time was investigated. Samples of 100 mL of Al$_2$O$_3$ slurry containing 3.0×10^{-2} M urea and various amounts of Zr-Ac were prepared by ball milling for 24 h, and 160 U of urease was then added. As shown in Fig. 2, slurries with Zr-Ac concentrations up to 1×10^{-3} M showed almost the same solidification onset time (2,300 s). However, the solidification onset time increased markedly (3,000 s) with addition of <1×10^{-1} M Zr-Ac. The addition of excess Zr-Ac delayed the shift of pH towards the alkaline region due to hydrolysis of Zr-Ac. Green bodies, which were solidified in a climate chamber at 27 °C and R.H. 98 % for 24 h, could be fabricated in all slurries, except those without Zr-Ac; some of green bodies were not completely solidified even after 24 h. Based on these results, the optimum amount of Zr-Ac was selected to obtain solidification of the slurries within 24 h.

3-3 Effects of Zr-Ac concentration on linear shrinkage and density

Linear shrinkage of the green bodies and the sintered bodies as a function of amount of Zr-Ac added to the slurries is shown in Fig. 3. Shrinkage of the green bodies increased with increasing amount of Zr-Ac. However, the degree of shrinkage of the green bodies was low, i.e., less than 2 % calculated from the mold size. Linear shrinkage of sintered bodies was about 12 %, except for
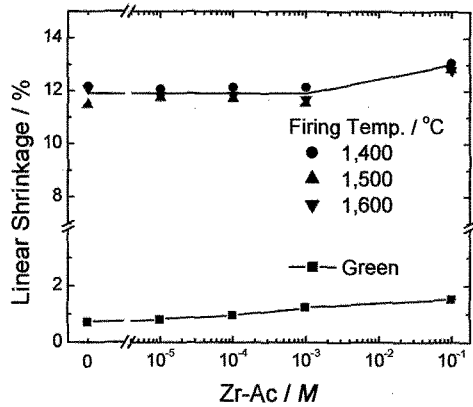
Fig. 3 Effects of Zr-Ac concentration on linear shrinkage of the green bodies and sintered bodies fired at 1,400, 1,500, and 1,600 °C.
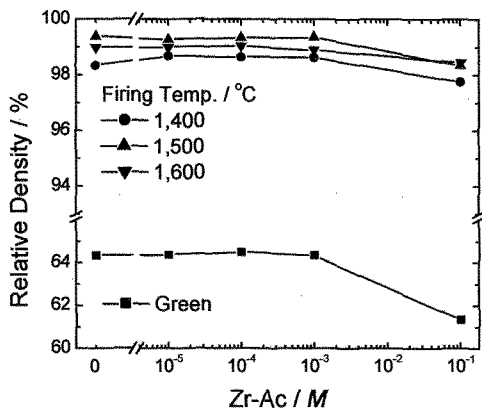

Fig. 4 Effects of Zr-Ac concentration on relative density of the green bodies and sintered bodies fired at 1,400, 1,500, and 1,600 °C.

Fig. 5 Microstructures of the polished and then thermally etched surfaces of the bodies, fired at 1,500 °C. (a) Without Zr-Ac, (b) 1×10^{-4}, and (c) 1×10^{-1} M Zr-Ac.

Fig. 6 Photograph of a green body (left) and a sintered body (right) fabricated by the proposed DCC method.

those fabricated with 1×10^{-1} M Zr-Ac for which the value was 13 %. This difference in shrinkage was considered to be due to the influence of acetic acid contained in Zr-Ac. The relative densities (R.D.) of the green bodies and the sintered bodies, which were the same bodies used to measure shrinkage, are shown in Fig 4. The R.D. was calculated from the theoretical density of 3.96 g cm^{-3} of Al$_2$O$_3$. The green bodies fabricated with addition of Zr-Ac from 0 M to 1×10^{-3} M had R.D. values of about 63.5 %, which is close to the random packing density. However, the density of green bodies fabricated with addition of 1×10^{-1} M Zr-Ac was 60.3 %. The R.D. of the sintered bodies obtained from the green bodies described above was the highest (> 99.3 %) at 1,500 °C. Sintered bodies sintered at 1,600 °C showed lower values than those sintered at 1,500 °C because of grain growth of Al$_2$O$_3$ particles. The addition of an excess amount of Zr-Ac (1×10^{-1} M) led to low densities for the green and sintered bodies. Due to the nature of Zr-Ac to froth well, the addition of large amounts of Zr-Ac to the slurry resulted in difficulties in de-airing in the vacuum chamber. Large numbers of pores were observed in the microstructure as described below.
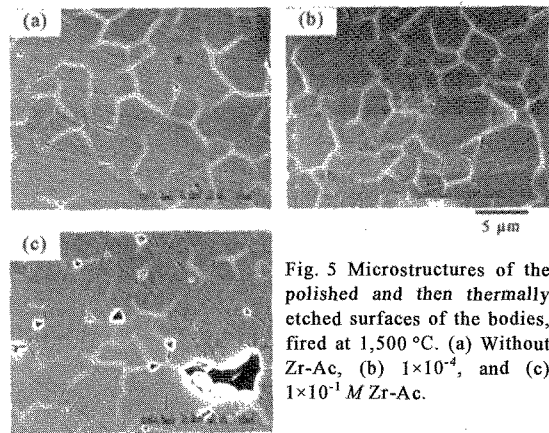
3-4 Observation of the sintered bodies by SEM

Figures 5 (a), (b), and (c) show the SEM images of the polished and then thermally etched surfaces of the sintered bodies fired at 1,500 °C. The SEM images of the sintered bodies made without Zr-Ac (a) and with 1×10^{-4} M Zr-Ac (b) indicated that few pores were present between the grain boundaries. However, the sintered bodies fabricated with from 1×10^{-1} M Zr-Ac contained many macro pores, which was attributed to the difficulty in de-airing.

3-5 Fabrication of sintered bodies using the complex mold by the proposed DCC method

Photographs of a green body and a sintered body with complex form, which were produced by this DCC process, are shown in Fig. 6. The green body and the sintered body were analogous to the mold used and showed no deformation. Further processing of the sintered body was not necessary, and it should be able to produce a product with complex form by taking shrinkage into consideration.

4. Conclusions

The DCC process using the enzyme-catalyzed urea-urease reaction for the aqueous Al$_2$O$_3$ slurry thickened with Zr-Ac was studied. The results of this study

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indicated that the following conditions were optimal:

1. The fluidity of the Al_2O_3 slurry was improved by the addition of Zr-Ac at concentrations from 1×10^{-5} to $1\times10^{-3} M$.

2. The optimal amount of urease was 160 U per 100 mL of Al_2O_3 slurry with $3.0\times10^{-2} M$ urea at 25 °C.

3. A good green body and sintered body were fabricated from slurries with the addition of a suitable amount of Zr-Ac.

Slurries containing a suitable amount of Zr-Ac could form good solidified green bodies (R.D. > 63.5%). Then, the sintered bodies produced by these green bodies had very high density (R.D. > 99.3%).

Acknowledgments

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