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Shaping of Alumina Body through an Eco-conscious Process - Direct Casting of Alumina Slurry by Hydrolysis of Aluminum Nitride -

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A new method for direct casting of aqueous alumina slurries has been developed. Aluminum nitride was added to high solid-loaded slurries, which were stabilized and fluidized by the addition of ammonium polyacrylate as a dispersant at pH 10. The dissolution of aluminum nitride into the slurry gradually increased the ionic strength due to the formation of various ionic species. The slurry coagulated, changing its properties from a viscous liquid to a homogeneous, rigid, green body. The fired density with 99 % theoretical density was obtained through this new direct casting method.
Key words: Aqueous alumina slurry, Aluminum nitride, Shaping, Direct casting, Eco-conscious process

1. INTRODUCTION

Alumina is a prime candidate for the production of structural ceramic parts. Shaping of this material and the preceding alumina powder preparation process are very important in the fabrication of alumina parts as defects introduced in the shaping process will normally remain in the final product even after a successful sintering process. Shaping through aqueous media is especially important in terms of environmental impact, safety, and cost. More recent direct casting methods [1], such as gel-casting [2, 3] and direct coagulation casting [4-7], are based on a colloidal process [8] controlled by the optimum conditions of processing factors: i) types of media and dispersant; ii) ceramic powder loading; and iii) the amount and molecular weight of the dispersant. Previously, we reported that the dispersion and fluidity of aqueous alumina slurries were enhanced by addition of zirconium acetate [9] or ammonium polyacrylate (PAA) [10, 11], and that there are optimum amounts and molecular weights of PAA for use in this process. Under optimum conditions, the green compact with theoretical density (T.D.) above 60 wt% could be obtained through the slip casting process using a plaster of Paris mold. However, the slip casting process had a number of difficulties, such as restriction of the number of molds that can be utilized and contamination of the compact from the mold. On the other hand, direct casting was superior to slip casting as shaping could be performed without any restriction of the mold.

We noted that the alumina slurry was solidified by increasing the ionic strength of its slurry because this markedly reduced the electrostatic repulsive force between the alumina particles. Aluminum nitride (AlN) forms various aluminum species by hydrolysis with changing pH: i.e., aluminum ions, aluminum oxide ions, aluminum hydroxide, and ammonium ions.

The present study was performed to elucidate the effects of AlN on the shaping of aqueous high solid-loaded alumina slurries dispersed and thickened using PAA. We measured the following processing factors: i) the elution rate of AlN into aqueous media; ii) the onset time of solidification of the slurry with differences in the amount of AlN added; and iii) the density and shrinkage of green and sintered compacts.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Alumina (Al_2O_3) used in this study was α-alumina (A-16 SG, Alcoa, PA, USA) with an average particle size of 0.5 μm. A commercial AlN powder (Grade H, Tokuyama Co., Yamaguchi, Japan) was used to control the ionic strength. PAA (average molecular weight 6,200) was prepared by neutralization of polyacrylic acid (Aldrich Chemical Co., WI, USA) with ammonium hydroxide.

2.2 Shaping process

Alumina slurries were prepared as follows: alumina powder was added to water containing various amounts of PAA, calculated in dry base weight relative to the alumina powder. The water used to prepare all of the slurries was distilled and purified using a Milli-Q system (Milli-Q Plus, Millipore Co., MA, USA). AlN powder was mixed with the slurries using a planetary mixer (MS-SNB-350N, Matsuo Ind., Osaka, Japan) for 150 s after ball milling of the slurries for 24 h. Then, the slurries were cast into plastic molds followed by standing in a climatic chamber with controlled humidity (97 %) and temperature (27 °C) for 24 h. Solidified compacts were air-dried at room temperature for 24 h. Green compacts obtained in this experiment measured 80 × 50 × 6 mm. Sintered compacts were obtained by firing the green compact at 1,500 °C for 2 h.

2.3 Measurements

To determine the amount of AlN eluted, 1 g of AlN was added to 50 mL of 1 wt% PAA aqueous solution followed by standing for various durations. Aluminum in the supernatant of the solution was determined using an ICP-AES (PS1000UV, Leeman Labs, NH, USA). The onset time of solidification of the slurry was determined by measurement of the storage modulus (G')

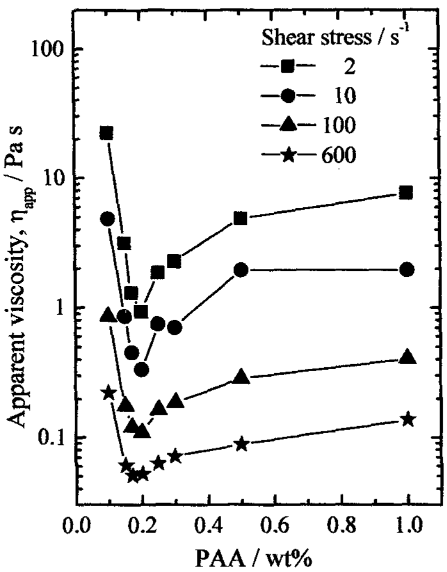

Fig. 1 Fluidity of the Al_2O_3 slurries in the presence of various amounts of PAA.

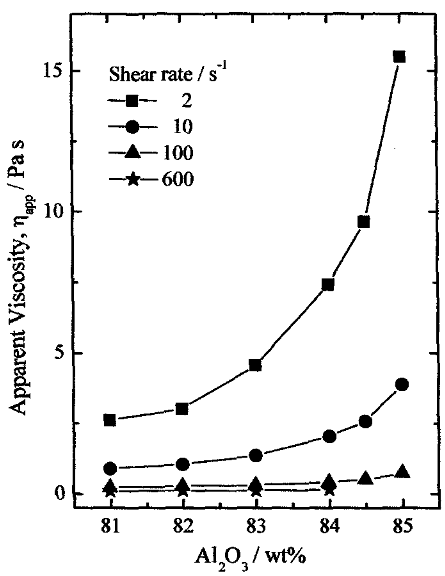

Fig. 2 Thickening of the Al_2O_3 slurries.

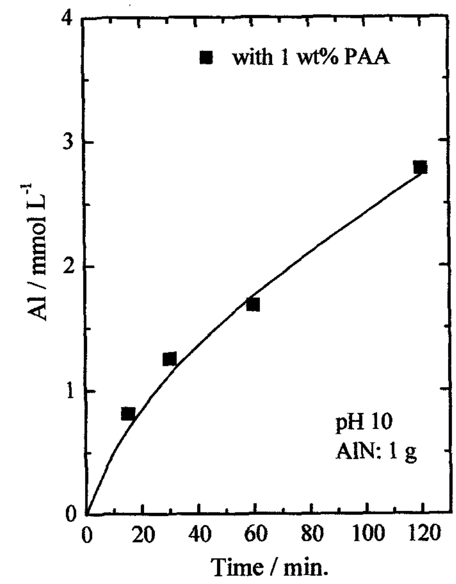

Fig. 3 Elution of AlN into the aqueous media.

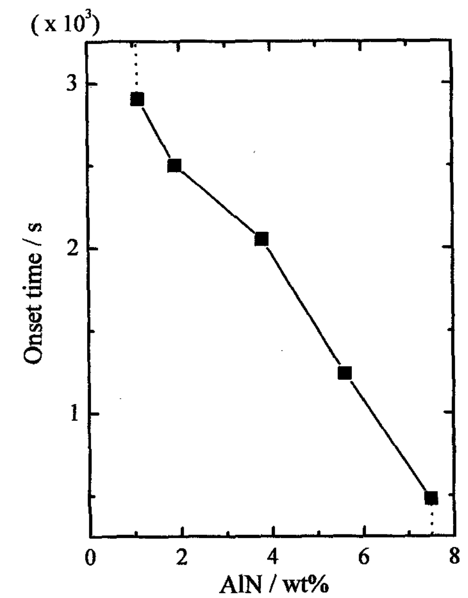

Fig. 4 The solidification onset time of the slurries in the presence of various amounts of AlN.

at 25 °C using a controlled stress rheometer (RS-150, Haake, Karlsruhe, Germany) with a double gap cylinder (DG-41). The densities of the green compacts were calculated from their size and weight. The fired densities were measured by the Archimedes method.

3. RESULTS AND DISCUSSION

3.1 Effects of PAA on fluidity of the slurry

A thickened slurry with fluidity was preferable for the direct casting method. Fig. 1 shows the apparent viscosity of the slurries in the presence of various amounts of PAA as a parameter of various shear rates. Apparent viscosity decreased markedly to a low value until 0.2 wt% of PAA and then increased gradually at each shear rate. This result indicated that addition of 0.2 wt% of PAA significantly enhances the fluidity of the slurries.

Fig. 2 shows the apparent viscosity of the slurries with 0.2 wt% of PAA as a function of Al_2O_3 solids loading. The apparent viscosity increased gradually until 84 wt% Al_2O_3 and then increased abruptly above this level. The thickening limit of the slurry with fluidity, which was preferable to the direct casting method, was found at 84 wt% (57 vol%) solids loading.

3.2 Solidification onset time

The elution behavior of AlN into aqueous media and the solidification onset time of the slurries, as the elution

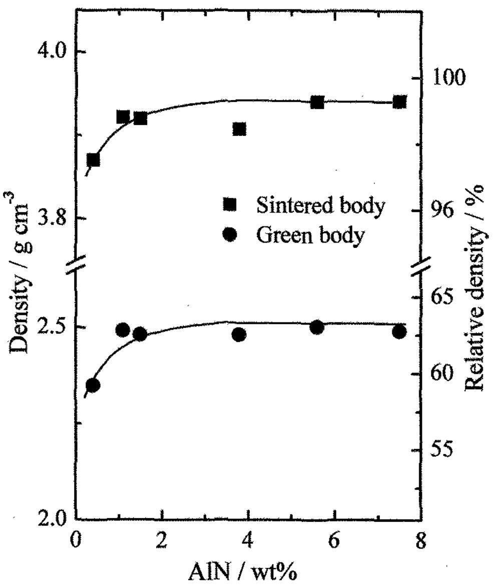

Fig. 5 Densities of green and sintered compacts.

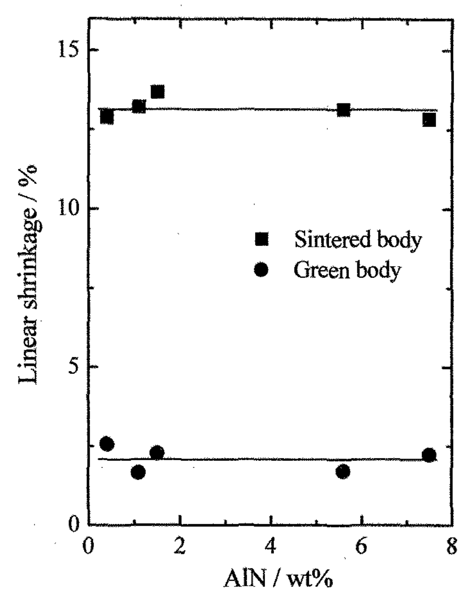

Fig. 6 Linear shrinkage of green and sintered compacts.

of AlN resulted in an increase in the ionic strength of the slurries, were most important parameters in the direct casting method. Fig. 3 shows the time dependence of the amount of AlN eluted into the aqueous media with 1 wt% PAA at pH 10. The amount of Al in the media increased gradually with elution time. This gradual increase represents a slow increase in the ionic strength. With addition of AlN to neutral aqueous media, no Al was detected in the supernatant by ICP, despite shifting pH to the alkaline region because of the formation of ammonium ions. For this reason, it was presumed that dissolved Al species formed a precipitate, such as aluminum hydroxide. PAA should play a role as an inhibitor of precipitate formation, i.e., a complex should be formed between aluminum ions and PAA. Unfortunately, the phenomena occurring in the media could not be clarified in detail in this experiment. These problems will be clarified in the near future.

Fig. 4 shows the effects of amounts of AlN added to the slurries containing 84 wt% Al_2O_3 on the solidification onset time. The onset time decreased linearly with increasing amount of AlN. However, with addition of AlN below 1.0 wt%, solidification required a few days. On the other hand, the slurries began to solidify almost immediately above 7.5 wt% AlN. The optimum amount of AlN was in the range of 1.0 to 7.5 wt% in dry base weight to the Al_2O_3 powder for direct casting.

3.3 Evaluation of green and sintered compacts

The green compacts were obtained by drying the solidified compacts fabricated under the conditions described above in climatic chamber with controlled humidity and temperature for 24 h, and then the green compacts were sintered at 1,500°C for 2 h. Fig. 5 shows the green and sintered densities of the compacts as a

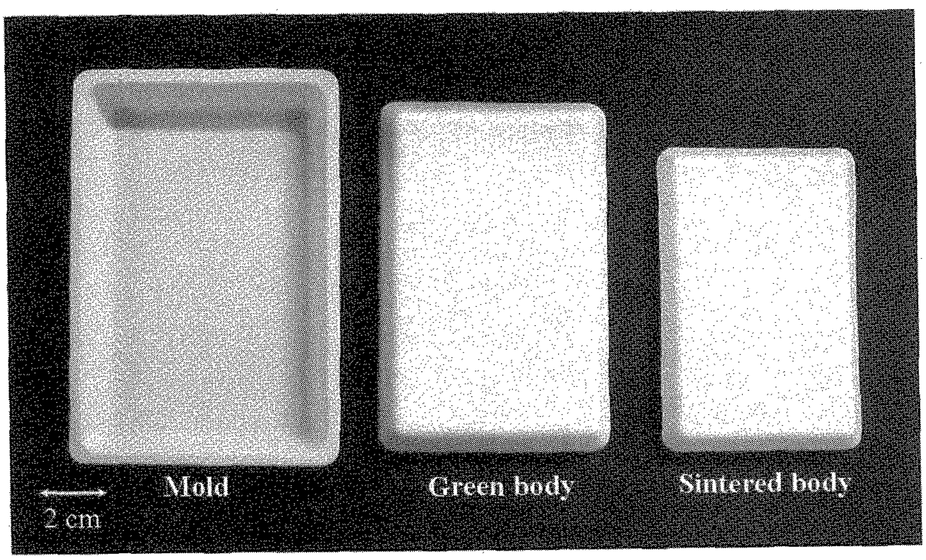

Fig. 7 Photograph of mold, and both green and sintered compacts.

function of the amount of AlN added to the slurries. All of the green densities showed almost the same value of 62.5 % T.D., indicating that a high degree of packing was achieved in the green compact. The sintered densities also represent the same values above 99 % T.D. The high sintered densities reflect the results obtained for the green compacts.

Fig. 6 shows the results of measurement of linear shrinkage for the green and sintered compacts, where linear shrinkage represents the difference in size between the mold and the green compact. The green compacts all showed almost the same shrinkage value of 2 %. These values were very small in the ceramic shaping process. The shaping developed in this experiment was regarded as a near-net-shaping process. The linear shrinkage between green and sintered compacts showed a constant value of 13 % for all compacts. The small degree of shrinkage of the sintered compact was attributable to the high packing density of the green compact, as described above.

Fig. 7 shows photographs of the mold, green, and sintered compacts. The compact shown in this photograph was fabricated through a slurry containing 1.0 wt% of AlN because it was preferable to add as little AlN as possible for fabrication of the compact. The addition of large amounts of AlN, resulting in residual AlN particles remaining in the slurry, would result in various defects in the sintered Al_2O_3 body.

4. CONCLUSIONS

In the new direct casting method developed in this study, AlN added to the Al_2O_3 slurry with PAA was effective as a starting reagent to induce solidification of the slurry. The dissolution of AlN into the slurry gradually increased the ionic strength because of the formation of various ionic species. As a result, the slurry coagulated, changing its properties from a viscous liquid to a homogeneous, rigid, green body. The degree of shrinkage of the green compact on drying was very small, and thus this was regarded as a near-net-shaping process. The fired density with 99 % theoretical density was obtained using this new direct casting method.

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