

## Direct Casting of Aqueous Alumina Slurries Using Increase of Ionic Strength by Addition of Yttria

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A new method has been developed for direct casting of aqueous alumina slurries. Yttria powder added to alumina slurries with PAA was effective as a starting reagent to induce solidification of the slurry. The addition of yttria to the alumina slurries just before casting gradually increased the ionic strength of these slurries, which were then coagulated. As a result, a homogeneous green compact was obtained. The relative density of the sintered compact was 99.5 % theoretical density (T.D.) and the compact had a bending strength of 480 MPa. The proposed method may provide the option to use a range of mold materials, the ability to make large parts with both thick and thin sections, and minimal molding defects. Key words: Aqueous alumina slurry, Yttria, Shaping, Direct casting, Eco-conscious process

### 1. INTRODUCTION

Recently, some new direct casting methods that are based on colloidal ceramic processing have been presented for the near-net-shape forming technique of complex ceramic parts, such as gel casting, direct coagulation casting, *etc.* [1, 2]. Gel casting is a new forming technique that involves the polymerization of a monomer in an aqueous or nonaqueous solvent forming a rigid, ceramic-loaded body that can be machined in the green state or formed directly in a complex mold [3, 4]. Although this process is very promising additive toxicity, extensive drying procedures, and problematic polymerization reactions, have proved difficult to overcome in many ceramic systems. The direct coagulation casting technique is another novel complex-shape-forming technique based on the time-delayed coagulation (destabilization) of initially stabilized suspensions, which had been poured previously into a complex-shaped mold. Gauckler *et al.* demonstrated that the destabilization was accomplished through the use of enzyme-catalyzed *in situ* reactions that shifted the suspension pH to the particle isoelectric point or increased the ionic strength, compressing the particle electrical double layer at a given pH, resulting in a rigid body with little or no polymer additives [5, 6]. The direct coagulation casting process has been successfully applied in the production of complex ceramic parts displaying homogeneous microstructure with minimal density gradients. Recently, we also reported a new direct casting method based on aqueous-acidic high solid-loaded alumina ( $\text{Al}_2\text{O}_3$ ) slurries stabilized with zirconium acetate [7]. Coagulation of the  $\text{Al}_2\text{O}_3$  slurries was accomplished by urea-urease enzyme reaction in the slurry at room temperature.

Preparation of ceramic slurry is one of the important processes in ceramic colloidal processing. The preparation of a thick slurry with high fluidity is needed to fabricate a fine green and sintered body. Aqueous ceramic processing is advantageous from the viewpoints of ecology, safety, and cost. It is well known that

ammonium polyacrylate (PAA) effectively enhances the dispersion and fluidity of aqueous  $\text{Al}_2\text{O}_3$  slurries [8-10]. In this study, we propose a new direct casting method of aqueous high solid-loaded  $\text{Al}_2\text{O}_3$  slurries stabilized by PAA. Addition of yttria ( $\text{Y}_2\text{O}_3$ ) to the  $\text{Al}_2\text{O}_3$  slurries just before casting gradually increased the ionic strength of these slurries, which were then coagulated. As a result, the homogeneous green compact was obtained.

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 Materials

$\text{Al}_2\text{O}_3$  (A-16SG, Alcoa, Pittsburgh, PA, USA), with a normal particle size of 0.3  $\mu\text{m}$  and a BET specific surface area of 10  $\text{m}^2 \text{g}^{-1}$ , was used as received to prepare the slurries. A commercial  $\text{Y}_2\text{O}_3$  powder (Nacalai Tesque Inc., Kyoto, Japan), with a normal particle size of 3.3  $\mu\text{m}$  and a BET specific surface area of 3.6  $\text{m}^2 \text{g}^{-1}$ , was used to control the ionic strength in the slurries. Ammonium polyacrylate (PAA) as a dispersant was prepared by neutralization of poly(acrylic acid) (average molecular weight 5000, Aldrich Chemical Company, Inc., Milwaukee, WI, USA) with  $\text{NH}_3$  aqueous solution. The water used to prepare all of the sample solutions was distilled and purified with a Milli-Q system (Milli-Q Plus, Millipore Corporation, Bedford, MA, USA).

#### 2.2 Processing

A fixed amount of PTFE balls, water, PAA, and  $\text{Al}_2\text{O}_3$  powder were put together in a polypropylene bottle and homogenized by milling for 24 h at room temperature. The pH of the slurries was adjusted at pH 10.0 with  $\text{NH}_3$  aqueous solution. The acidity of suspensions was determined with a pH/ion/conductivity meter (Accumet 50, Fisher Scientific Co., Pittsburgh, PA, USA) using a glass combination electrode (Model 8172 ROSS Sure-Flow<sup>®</sup> pH Electrode, Orion Research, Inc., Beverly, MA, USA). After ball milling, an appropriate amount of  $\text{Y}_2\text{O}_3$  powder was added to 20 mL of the  $\text{Al}_2\text{O}_3$  slurry and mixed using a planetary mixer (MS-SNB-350N, Matsuo Ind., Osaka, Japan) for

150 s. The slurries were then de-aired under vacuum for 3 min and cast into nonporous polypropylene molds ( $80 \times 50 \times 6$  mm). The slurries were solidified at  $27^\circ\text{C}$  and R.H. of 98% in a climatic test chamber (MTH-2200, Sanyo Electric Co., Osaka, Japan) for 24 h. The green bodies were removed from the molds and dried at room temperature for 24 h. They were then fired in air by heating at a rate of  $1^\circ\text{C min}^{-1}$  to  $600^\circ\text{C}$ , at which temperature they were held for 2 h. The temperature was then elevated to the firing temperature ( $1400$  to  $1600^\circ\text{C}$ ) at  $2^\circ\text{C min}^{-1}$  and held there for 2 h in air to obtain the fired bodies.

### 2.3 Characterization

Well-dispersed slurries with low viscosity were used. To characterize the flow behavior of the slurries, shear rate versus shear stress curves (flow curves) were determined using a controlled stress rheometer (RS-150, Haake, Karlsruhe, Germany) equipped with either a parallel plate sensor (20, 35, or 60 mm in diameter) or a double gap cylinder sensor (DG41). The coagulation behavior of slurry was evaluated by measurement of the storage modulus ( $G'$ ) using the rheometer. All measurements were carried out at  $25^\circ\text{C}$  unless otherwise noted. Green densities were determined by measuring the dimensions and weights of the samples and are given as relative densities based on the theoretical density of  $\text{Al}_2\text{O}_3$ ,  $3.97 \text{ g cm}^{-3}$  [11]. The fired densities were measured by the Archimedes method. All data points represent the average of five density measurements. The microstructure of the fired compacts was observed by scanning electron microscopy (SEM; S-4300, Hitachi, Ltd., Tokyo, Japan) equipped with an energy dispersive X-ray micro analyzer (EMAX ENERGY EX-220, Horiba, Ltd., Kyoto, Japan). X-ray diffraction analysis (XRD) and bending strength were determined with an X-ray diffractometer (MO3XHF22, MAC Science Co., Ltd., Yokohama, Japan) and a bending test machine (Tensilon UCT-5T, Orientec, Tokyo, Japan), respectively. To determine the amount of  $\text{Y}_2\text{O}_3$  eluted, 1 g of  $\text{Y}_2\text{O}_3$  was added to 50 mL of the aqueous solution with/without 1 wt% PAA at pH 10.0 followed by standing for various durations. Yttrium concentration in the supernatant of the suspension was determined using an ICP-AES (PS1000UV, Leeman Labs, Inc., Hudson, NH, USA).

## 3. RESULTS AND DISCUSSION

### 3.1 Flow behavior of $\text{Al}_2\text{O}_3$ slurries with PAA

High solid-loaded slurries with good fluidity are preferable for colloidal processing. The apparent viscosities ( $\eta_{\text{app}}$ ) of the 80 wt%  $\text{Al}_2\text{O}_3$  slurries at pH 10.0 as a function of PAA concentration are shown in Fig. 1. The value of  $\eta_{\text{app}}$  decreases to a low value at 0.2 wt% PAA and then increases. Figure 2 shows the relation between  $\eta_{\text{app}}$  and solids loading of  $\text{Al}_2\text{O}_3$ . The value of  $\eta_{\text{app}}$  gradually increased until 84.5 wt%  $\text{Al}_2\text{O}_3$  and then increased abruptly. The thickening limit of the slurry with fluidity, which was preferable to that obtained by the direct casting method, was found at 84.5 wt%  $\text{Al}_2\text{O}_3$ .

### 3.2 Solidification behavior of slurries

Figure 3 shows the effects of amount of  $\text{Y}_2\text{O}_3$  added to the 84.5 wt%  $\text{Al}_2\text{O}_3$  slurries on the solidification

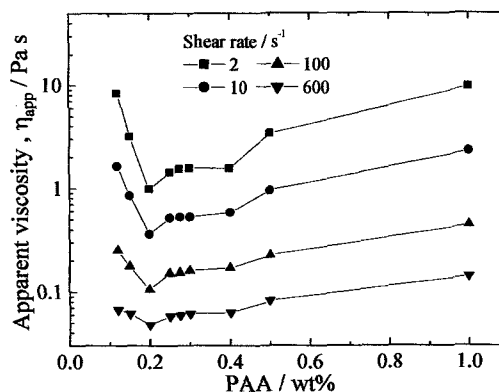


Fig. 1 Apparent viscosity of 80 wt%  $\text{Al}_2\text{O}_3$  slurries as a function of PAA concentration

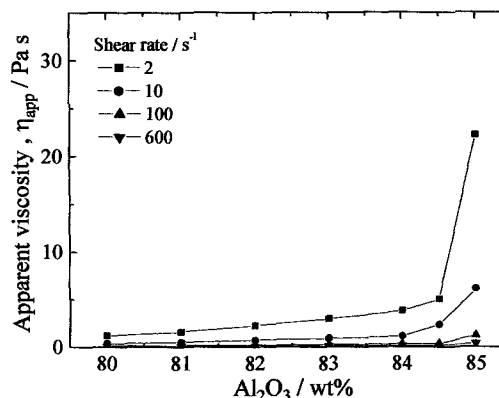


Fig. 2 Apparent viscosity of  $\text{Al}_2\text{O}_3$  slurries with optimum amount of PAA as a function of solids loading

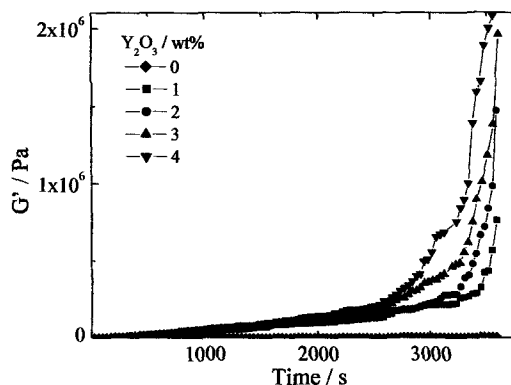


Fig. 3 Coagulation time vs.  $G'$  curves for 84.5 wt%  $\text{Al}_2\text{O}_3$  slurries as a function of  $\text{Y}_2\text{O}_3$  amount

behavior. The storage modulus ( $G'$ ) increased with increasing amount of  $\text{Y}_2\text{O}_3$ . However, with addition of  $\text{Y}_2\text{O}_3$  at concentrations below 1.0 wt%, solidification required several days. On the other hand, the slurries started to solidify immediately with addition of  $\text{Y}_2\text{O}_3$  above 5 wt%. The optimum amount of  $\text{Y}_2\text{O}_3$  was found in the range of 1 to 4 wt% in dry base weight relative to the  $\text{Al}_2\text{O}_3$  powder for direct casting. The elution behavior of  $\text{Y}_2\text{O}_3$  into aqueous media and the solidification behavior of the slurries, as the elution of  $\text{Y}_2\text{O}_3$  resulted in an increase in the ionic strength of the slurries, were the most important parameters in the direct casting method. Figure 4 shows the time dependence of the amount of  $\text{Y}_2\text{O}_3$  eluted into the

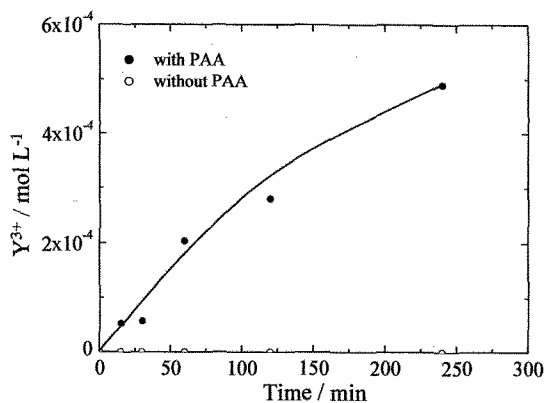


Fig. 4 Elution of  $Y_2O_3$  into aqueous media with or without 1 wt% PAA at pH 10.

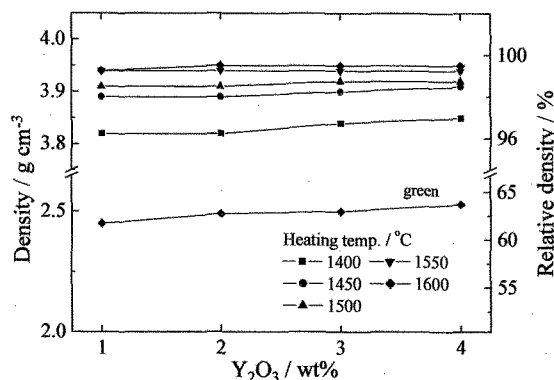


Fig. 5 Densities of green and fired compacts at various temperatures as a function of  $Y_2O_3$  amount

aqueous media with 1 wt% of PAA at pH 10.0. The amount of yttrium in the media increased gradually with elution time. This gradual increase represents a slow increase in the ionic strength. On the other hand, with addition of  $Y_2O_3$  to the aqueous media without PAA at pH 10.0, yttrium was not detected in the supernatant of the media by the ICP-AES. The solubility product,  $K_{sp}$ , for yttrium hydroxide,  $Y(OH)_3$ , is very low with a values of  $8.0 \times 10^{-23}$  at  $25^\circ C$  [12]. Thus, it was presumed that dissolved yttrium species formed a precipitate, such as  $Y(OH)_3$ , at pH 10.0 and yttrium was not detected without PAA. PAA should play a role as an inhibitor of precipitate formation, *i.e.*, a complex should be formed between an yttrium ions and PAA molecules. In addition, the yttrium-PAA complex should destabilize the initially stabilized suspensions. Unfortunately, the phenomena occurring in the media could not be clarified in detail in this experiment and will be addressed in the near future.

### 3.3 Effects of amount of $Y_2O_3$ on forming and sintering

The green compacts were obtained by drying of the solidified compacts, fabricated under the conditions described above, in a climatic test chamber with controlled humidity and temperature for 24 h. The green compacts were then sintered. Figure 5 shows the effects of the amount of  $Y_2O_3$  added in the  $Al_2O_3$  slurries on the densities of the green and sintered bodies fired at various temperatures. 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

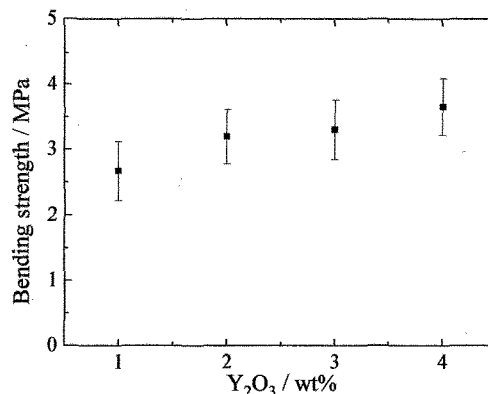


Fig. 6 Bending strength of green compacts as a function of  $Y_2O_3$  amount

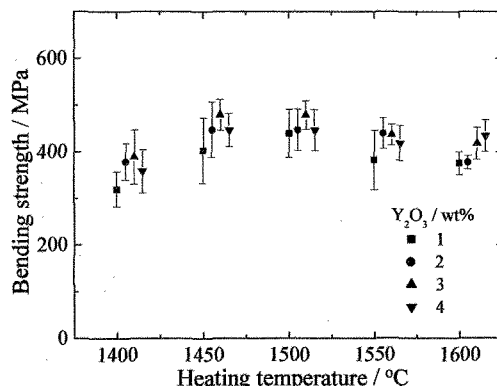


Fig. 7 Bending strength of fired compacts at various temperatures as a function of  $Y_2O_3$  amount

compact. The fired densities of  $Al_2O_3$  bodies increased with firing temperature. At  $1400^\circ C$ , the densities of the fired bodies increased with increasing amount of  $Y_2O_3$  added. However, at  $> 1550^\circ C$ , the densities were almost constant and independent on the amount of  $Y_2O_3$  added. Higher sintered densities of  $Al_2O_3$  are attained, reaching 99.5% T.D., after firing at 1550 and  $1600^\circ C$ . The high sintered densities reflect the results obtained with the green compacts. The bending strength of the green body versus amount of  $Y_2O_3$  added is plotted in Fig. 6. The strength of the green body increased with increasing amount of  $Y_2O_3$  added. The yttrium-PAA complex and/or  $Y(OH)_3$  should play a role as a binder. Figure 7 shows the bending strength of the fired body versus amount of  $Y_2O_3$  added at several temperatures. The strength of the fired body showed a maximum at  $1450-1500^\circ C$ . At all fired temperatures, addition of 2 to 3 wt%  $Y_2O_3$  resulted in maximum at strength. YAG ( $Al_5Y_3O_{12}$ ) was found in the fired body at  $> 1450^\circ C$ , as shown in Fig. 8. Figure 9 shows a SEM image and the distribution of Al and Y in  $Al_2O_3$  sintered compact with addition of 3wt%  $Y_2O_3$  powder heated at  $1450^\circ C$ . Yttrium was found in large  $Y_2O_3$  grains and the  $Al_2O_3$  phase. Usually, the presence of large particles decreases the strength. However, the  $Al_2O_3$  sintered compact produced with addition of 3wt%  $Y_2O_3$  powder heated at  $1450^\circ C$  showed a bending strength of 480 MPa (Fig. 7). YAG formation at the  $Al_2O_3$  grain boundary might enhance the strength. The detail will be clarified in the near future.

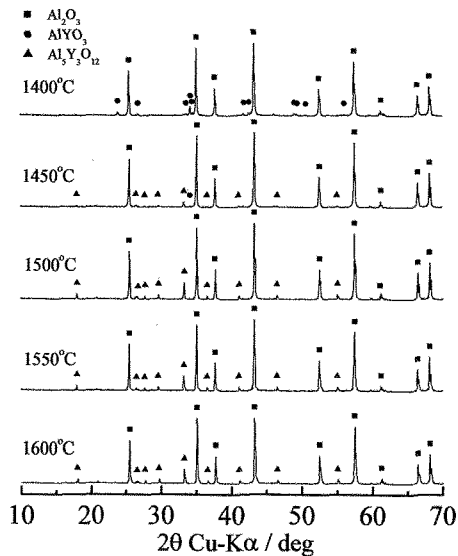


Fig. 8 XRD patterns at various heating temperatures.  $\text{Al}_2\text{O}_3$  with 3 wt%  $\text{Y}_2\text{O}_3$

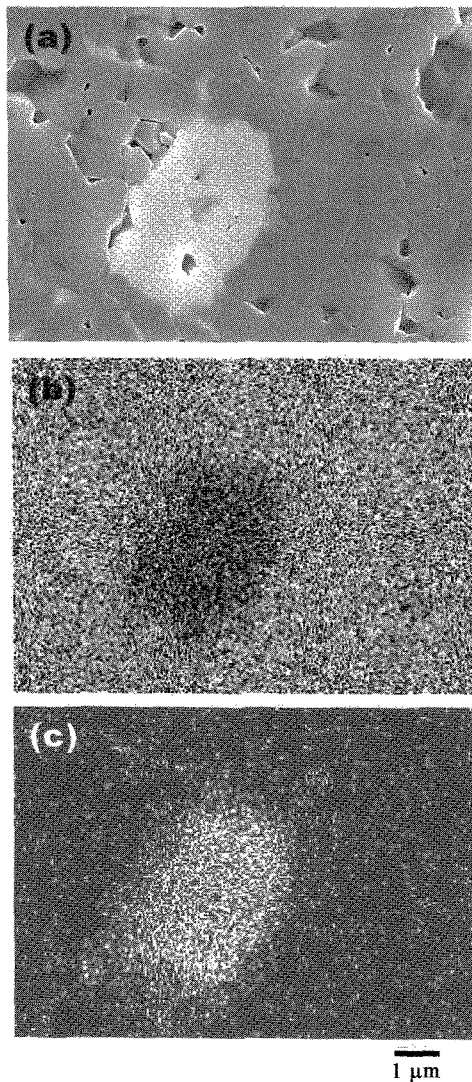


Fig. 9 SEM image (a) and X-ray map of fired  $\text{Al}_2\text{O}_3$  compact with 3wt%  $\text{Y}_2\text{O}_3$  heated at  $1450^\circ\text{C}$ . X-ray map for Al (b) and Y (c).

#### 4. CONCLUSIONS

In the new direct casting method developed in this study,  $\text{Y}_2\text{O}_3$  added to the  $\text{Al}_2\text{O}_3$  slurry stabilized with PAA was effective as a starting reagent to induce solidification of the slurry. The proposed method was suitable for near-net-shaping because of the very small degree of linear shrinkage ( $< 2\%$ ) of the green body in the drying process. The relative density of the sintered compact was 99.5 % T.D. and the bending strength was 480 MPa. The proposed method provides the option to use a range of mold materials, the ability to make large parts that have both thick and thin sections, and minimal molding defects.

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