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Control of high solid content yttria slurry with low viscosity for gelcasting

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Abstract

In order to fabricate ceramics using yttria powder which is an expensive rare earth compound, it is necessary to employ near net shape technique, such as gelcasting. Gelcasting, a technique which utilizes in situ polymerization of acrylamide monomers, needs high solid content slurry. However, slurry preparation is difficult because fine particles aggregate easily. This investigation was aimed at studying the effects of amount of dispersant and specific surface area on the dispersion of aqueous yttria slurries, using a rheological measurement. The viscosity measurement of 45 vol% slurry prepared from smaller specific surface area particles of yttria indicated that dispersant dosages of 1.45 mass% will give the lowest slurry viscosity. Near net-shaped parts of yttria have been successfully formed by gelcasting, using this slurry. The green bodies obtained were practically no cracks.

Keywords: Yttrium oxide; Gelcasting; Viscosity; High solid loading slurry

1. Introduction

Cold Isostatic Pressing (CIP) has been utilized in the field of ceramics and powder metallurgy as an effective powder compacting process. Ceramics having high degree of green density and uniformity of packing density can be fabricated by means of CIP. However, for large scale industrial production by this technique, a lot of waste powder is generated during processing, which leads to an increase in cost apart from environmental hazard. Slip casting and injection molding, as known as near net-shape technique, have considerable problem, such as solidification time lag between inside and outside of the green body produced, uneven density distribution, defects and cracks in the ceramics [1,2].

On the other hand, gelcasting [3–5] is known to form desirable complex shape using a little organic compound and to apply almost the same slurry preparation as that of the latter two techniques. However, it is necessary to prepare high solid content slurry, as the slurry density defines the green density of the formed ceramic material. As smaller particles have a tendency to aggregate easily, polymer dispersant has been employed to stabilize particle dispersion in the slurry by steric repulsive force. It has been reported by Nagata that slurry viscosity rapidly decreases with increasing amount of dispersant, and then further increases slowly [6]. Moreover, minimum viscosity value is required in order to have a good dispersion state in the slurry.

Yttrium oxide, an expensive rare earth compound, has been widely used in the areas of luminescence [7], translucent [8,9] and high temperature structural materials, owing to its excellent optical properties, thermostability, etc. Gelcasting is a generic process based on ideas from traditional ceramic process and polymer chemistry can be effectively utilized for suitable fabrication of near-net shape yttria ceramics. Dispersion of the powders in the gelcasting solution is an important process that must be controlled in order to produce castable suspension with desirable high solids loading. Achieving a stable suspension with high solid concentration and in terms of minimum viscosity is most desirable for gelcasting. It is most difficult to get high solids loading slurry, particularly with yttria powder. In this paper, the effects of specific sur-

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face areas and the amount of dispersant on the slurry viscosity have been examined in detail. As a result, 45–60 vol% yttria slurry was achieved with minimum viscosity, which is necessary for gelcasting of yttria. The corresponding data are compared with green body casted by the above technique.

2. Experimental

Two yttria powders were procured from Shin-Etsu Chemical Co. Ltd., Japan. The particle size distribution and specific surface area of the powders were measured with Zetasizer $3000HS_A$ (Malvern Instruments Inc., USA) and Micromeritics Gemini 2375 (Shimadzu Co., Kyoto, Japan), respectively. The geometric surface area of particle was calculated as follows [10]:

$$S_g = 6/\rho D \quad (1)$$

where S_g, ρ, D are the geometric surface area, density (5.03 g/cm^3) and particle diameter, respectively.

The surface roughness factor R_n was calculated as a ratio of real surface area (S_r) and geometric surface area (S_g) by utilizing equation:

$$R_n = S_r/S_g \quad (2)$$

A premix solution was prepared by dissolving an organic monomer, methacrylamide (MAM, Wako Chemical, Osaka, Japan), a cross-linker, *N,N′*-methylenebisacrylamide (MBAM, Wako Chemical, Osaka, Japan) and a polymer dispersant, ammonium poly (carboxylic acid) in distilled water. The yttria powder was suspended in the premix solution and ball-milled for 16 h. After ball-milling, the slurry was degassed for 2 min (2000 rpm, MX-201 THINKY Co.). The viscosity of the slurry was measured with a B type viscometer at shear rate in the range of 2.97–14.84 s^{-1}. The polymerization of the above slurry was initiated by adding an initiator, ammonium persulfate (APS, Wako Chemical, Osaka, Japan). Immediately after the addition of the initiator, the reaction was accelerated with a catalyst, *N,N,N′,N′*-tetramethyl ethylenediamine (TEMED, Wako Chemical, Osaka, Japan). The slurry was then casted into a mold made of Teflon. The solidified green body was demolded and dried in a controlled humidity chamber (FX206P, ETAC, Tokyo, Japan) after 5 h later the addition of the initiator and the catalyst. The dried body was heated until the polymer is completely decomposed using an electronic furnace (KYOEI DENKI SEISAKUSHO, Gifu, Japan) in an air atmosphere, and then sintered at 1800 °C.

The fractured surfaces of dried ceramic bodies were observed with SEM (Model JSM-6100, JEOL Ltd., Tokyo, Japan). Densities of sintered bodies were determined by using Archimedean method.

3. Results and discussion

3.1. Characterization of yttria powders

The average particle sizes determined by the dynamic light scattering technique were 1.08 and 0.90 μm for Yttria A and Yttria B powder, respectively. The specific surface areas measured by BET method for Yttria A and Yttria B were 11.09 and 4.60 m^2/g, respectively. The geometric surface areas and the roughness factor of Yttria A and Yttria B samples were calculated using Eqs. (1) and (2), and were found to be 1.10 and 1.33 m^2/g, 10.08 and 3.46, respectively.

3.2. Rheological characteristics

Fig. 1 shows the effect of the amount of dispersant on the viscosity of 35 and 40 vol% slurries consisting of high specific surface area yttria particle (Yttria A). It was observed that the slurry viscosity strongly depends on the amount of dispersant. In case of the 35 vol% slurry, the addition of 0.83 mass% dispersant dosages makes the slurry viscosity minimum. Further, the slurry viscosity rapidly increases with the increase in the amount of dispersant up to 1.29 mass%. In the case of 40 vol% slurry, the lowest viscosity was obtained by adding 1.45 mass% dispersant dosages.

Fig. 2 shows the viscosity of 42 vol% slurry with low specific surface area yttria particle (Yttria B) as a function of dispersant dosages. On addition of 0.55 mass% dispersant, it shows the lowest slurry viscosity. The viscosity increased with increasing concentration of dispersant up to 4.00 mass%.

Fig. 3 shows the viscosity of the slurry containing Yttria A and Yttria B as a function of shear rate. The dispersant dosages were 1.45 and 0.55 mass% for Yttria A and Yttria B, respectively. Yttria B slurry shows a tendency to have low viscosity despite the high solid content.

The roughness factor (R_n) for Yttria A, calculated by using Eq. (2) was found to be extremely large. The surface of this

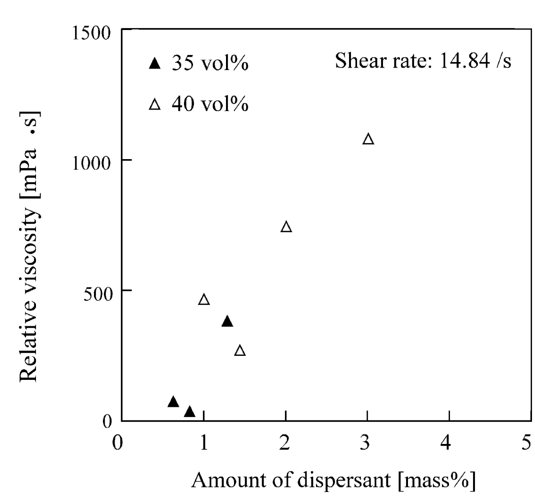


Fig. 1. Effect of the amount of dispersant on the viscosity 35 and 40 vol% slurries with high specific surface area Yttria A.

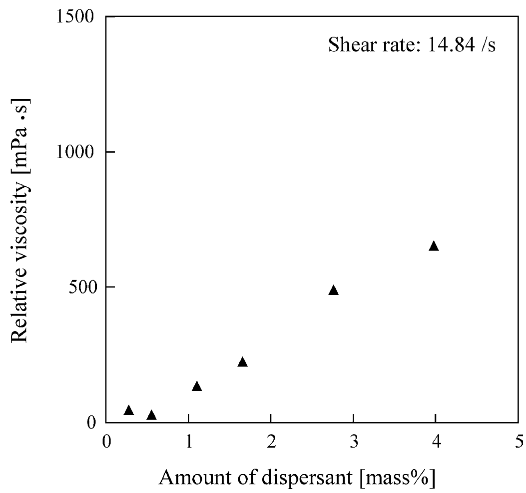


Fig. 2. Effect of the amount of dispersant on the viscosity 42 vol% slurry with low specific surface area Yttria B.

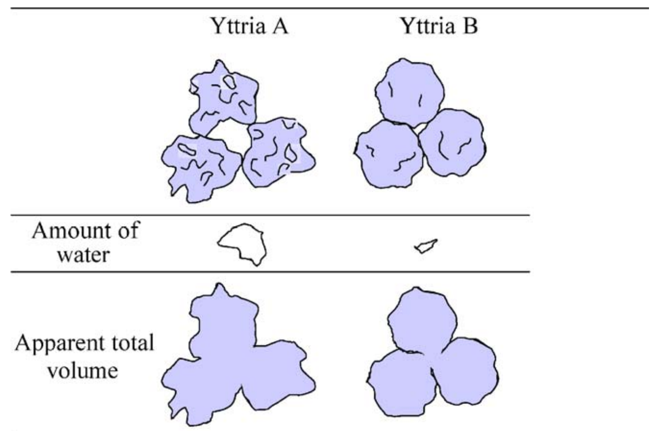
particle should have a high roughness and some pores, compared to that of Yttria B particle.

Figs. 1 and 2 clearly show optimum dosages of dispersant, which were found to be 1.45 and 0.55 mass% for Yttria A (40 vol%) and Yttria B (42 vol%), respectively. Fig. 3 further shows that the addition of optimum dosages of dispersant, Yttria B slurry had lower viscosity than that of Yttria A even at each optimum dosage of dispersant. Therefore, using lower specific surface area particle turned out to be suitable for a castable slurry of yttria.

Fig. 4 shows the viscosity of 45 vol% slurry containing Yttria B as a function of the amount of dispersant. The lowest slurry viscosity was obtained with 0.55, and 1.45 mass% dispersant at shear rate of 2.97 and 14.84 s^{-1}, respectively. Furthermore, the slurry viscosity rapidly increased with increasing amount of dispersant.

In this study, a difference between specific surface areas of A and B particles strongly affects the viscosity in high solid content slurry. It is thought that the low specific surface area

Table 1
Vacancies formed among particles and apparent total volume



particles B hold smaller amount of water among the particles than high ones A as illustrated in Table 1. That is, higher solid content slurry can be prepared owing to a larger volume of free water. Therefore, high concentration slurry could be prepared by the Yttria B powder having lower specific surface area but smaller primary particle size than Yttria A.

3.3. Forming characteristic

The slurry of 45 vol% using low specific surface area particle (Yttria B) was prepared. The optimum dosages of dispersant turned out to be 0.55 or 1.45 mass% as shown in Fig. 4. However, the slurry with 0.55 mass% dispersant showed very high viscosity during molding. That may be the reason why the slurry with 0.55 mass% was unsuitable for casting. Therefore, actual optimum amount of dispersant was estimated to be 1.45 mass%. Table 2 shows the number of cracks on the green bodies after drying and/or dewaxing. It has been observed that green bodies can be more easily fabricated from low specific surface area powder A than powder B.

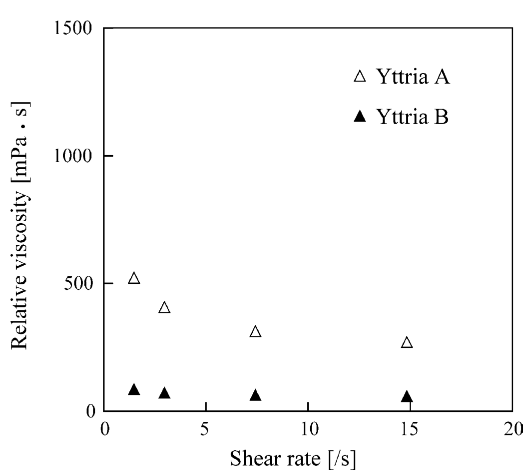


Fig. 3. The viscosity of Yttria A and Yttria B slurry with 1.45 and 0.55 mass% dispersant as a function of shear rate.

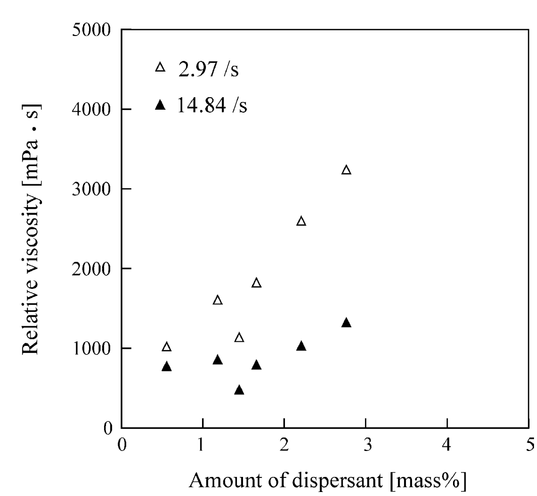


Fig. 4. The viscosity of 45 vol% slurry as a function of the amount of dispersant at shear rate 2.97 and 14.84 /s.

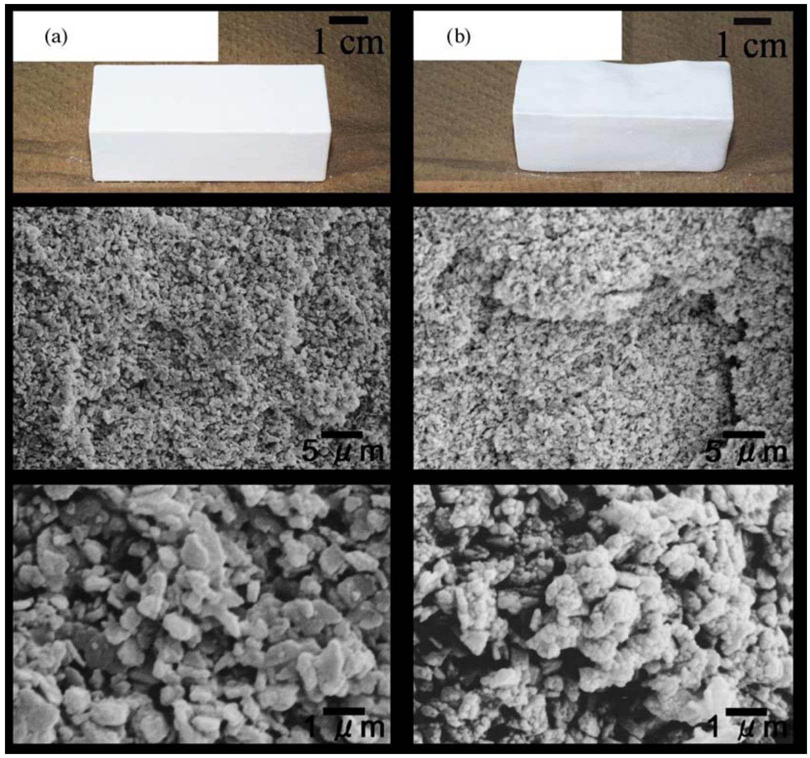


Fig. 5. Photographs of appearance and SEM images of fracture surfaces of green bodies after drying with amount of dispersant (a) 1.45 mass% and (b) 2.21 mass%.

Fig. 5a and b show SEM micrographs of fractured surfaces of in situ solidified 45 vol% Yttria B slurries with 1.45 and 2.21 mass% dispersant. The small particles ranging from 100 to 200 nm were found on both surfaces. It can be observed from Fig. 5a, that the fractured surface of the green body prepared from the slurry with 1.45 mass% dispersant was comparatively smooth. On the other hand, the fractured surface with 2.21 mass% dispersant was very rough and also the fracture occurred along the cluster of small particles. Fig. 6 shows the densities of sintered bodies prepared from the slurry containing 45 vol% yttria with different amounts of dispersant. In the case of the addition of 1.45 mass% dispersant, it showed the highest sintered density, 4.92 g/cm^3.

At the addition of the optimum dispersant dosages estimated from the rheological measurement, the well-dispersed slurry could be prepared and also the green body without cracks was obtained the high packing density of sintered body can be achieved. It should be emphasized that the addition of excess dispersant caused particle aggregation in the green body.

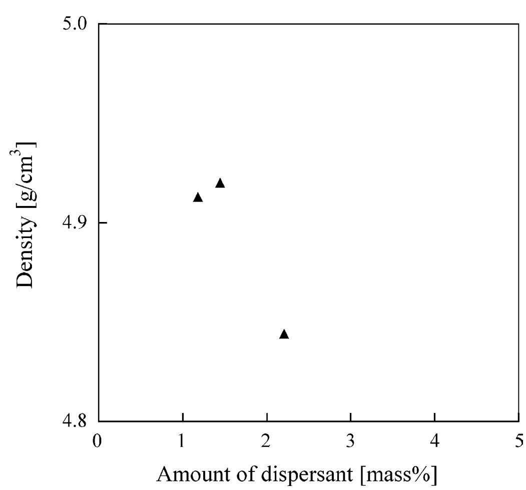


Fig. 6. Sintered density measured by Archimedian method as a function of amount of dispersant.

Table 2
The number of the cracked green bodies after drying or dewaxing

	Yttria A		Yttria B	
	35 vol%	40 vol%	42 vol%	45 vol%
No cracks	2	1	4	3
Cracks				
After drying	0	4	10	0
After dewaxing	3	6	2	1
Impossible to form	0	0	1	0

4. Conclusions

The followings are the conclusions drawn based on this investigation:

1. High solids content yttria slurry (45 vol%) which is necessary for gelcasting can be achieved using low specific

surface area particle and addition of the optimum amount of dispersant and the slurry had castable low viscosity.
2. It was clear that the slurry was well dispersed by SEM observation of the fractured surface and also the green body had no cracks. The high sintered density can be achieved.

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