Porous mullite nanopowder for slurry preparation of material direct writing by sol-gel method

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Nanoporous ultrafine powders of mullite with a stoichiometric composition were successfully prepared by controlling the agglomeration behavior of the sols prepared from molecular-designed precursor solution. Aging of the sols in the solvents with low dielectric constant, such as butylalcohol, resulted in the coarse flocculation of the primary colloidal particles to form nanoporous ultrafine precursor powders for the slurry to apply material direct writing. These precursor nanopowders crystallized into orthorhombic mullite powder with high surface area even after high temperature calcination at 1400 °C. The nanoporous structure of the precursor powder was successfully maintained in the thin films deposited by spin-coating from the sol of the nanoporous mullite precursor powders calcined at 800 wit °C with different oxide concentrations. As a result, nanoporous mullite ceramic thin films with a stoichiometric composition was prepared. The nanostructure of the resultant porous thin films were observed by AFM to show the relatively smooth surface with RMS values less than 3 nm.
Key words: Materials Direct Writing, Mullite, Nanoporous Powders, Thin Film,

1. INTRODUCTION

Stoichiometric mullite ($3Al2O_3 \cdot 2SiO_2$) is consisted of relatively high covalent Al_2O_3 and SiO_2 and, therefore, is very promising for a high-temperature structural material because of its superior mechanical properties compared with a silicon nitride or a silicon carbide ceramics even under the oxidizing atmosphere [1, 2]. The excellent high-temperature mechanical properties such as high creep resistance and high mechanical strength could be applied for high-temperature porous filters and catalyst worked at high temperatures, if very porous ceramics with high purity, homogeneity and high crystallinity were prepared below eutectic temperature of a mullite (1585 °C). So far, many preparation methods have been reported [3, 4, 5]. However, it is very difficult to prepare a stoichiometric mullite powder with high purity and homogeneity. The authors successfully prepared a stoichiometric mullite powder with high purity and homogeneity as well as the high specific surface areas from molecular-designed Al,Si-double alkoxide [6]. The surface areas of the mullite powders are affected by the compositions and a stoichiometric mullite precursor powder showed a very high surface area after calcination at elevated temperatures below 1400 °C [7]. The primary particles precipitated by the hydrolysis of the precursor solution could form agglomerates during aging and drying steps to increase the surface areas of the resultant calcined powders. Therefore, ultrafine xerogel powders would change their agglomerate structures depending upon the aging and drying conditions, leading to the control of the specific surface areas of the resultant nanoporous mullite powders.

This paper describes the relation between agglomeration behavior and the specific surface areas of the resultant nanoporous mullite powders and the nanostructure of the thin films deposited from the slurry of the nanoporous mullite precursor powder for the Materials Direct Writing (MDW) on the substrate.

Mullite also exhibits low dielectric constant and relatively low thermal expansion coefficient, and therefore, is useful as a substrate for high-speed computer and then the candidate material of thin film insulator with very low dielectric constant. This paper also focuses the basic research for deposit the nanoporous thin films on a LTCC substrates by MDW.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of nanoporous ultrafine powders.

The preparation method of precursor sols was described elsewhere [8]. After the hydrolysis of the precursor solution for 5 minutes, different kinds of solvents (mainly water, ethanol or iso-butanol) with different dielectric constants, which were prepared by changing the mixing ratio of water to ethanol, were added to the sols to control the agglomeration behavior of the sols during aging for one hour. Precursor sols were dried at 110 °C for 48 hours in an electric furnace or spray-dried at 200 °C to obtain xerogel precursor powders. These xerogel powders were pulverized for 3 minutes using alumina mortar and pestle, followed by the calcination at different temperatures for two hours up to 1400 °C.

2.2 Characterization.

The specific surface areas of calcined powders were measured by BET method. N_2 gas

and liquid nitrogen were used as an adsorbing gas and coolant, respectively. The morphology of the calcined powders were observed by scanning electron microscope (SEM) and the size distribution of pores were measured by mercury pore sizer. The size distribution of the nanoporous ultrafine powders were measured by using dynamic light scattering method. Planetary mill and zirconia beads of 2 mm were used to pulverize the nanoporous precursor powders calcined at 800 °C for 2 h. Surface morphology of the thin film was observed by Atomic Force Microscope (AFM).

3. RESULTS AND DISCUSSIONS
3.1 Solvent effect during aging and drying

Effect of the solvents on the surface area of the resultant powders was studied by adding the different kinds and/or amount of solvents after hydrolysis of the precursor solution. The agglomeration behavior of the ultrafine primary particles was strongly affected by the thickness of the electrical double layer. Thickness of the double layer on the colloidal particles is expressed by the equation (1) [9].

$$1/\kappa = (\varepsilon_0 \varepsilon RT/2F^2CZ)^{1/2} \qquad (1)$$

where F is Faraday constant, C and Z are the concentration and valence of the counter ions respectively, ε_0 and ε is the dielectric constant in vacuum and solvent, R and T are gas constant and absolute temperature. Figure 1 shows change in the surface area of the powders calcined at 1400 °C, prepared by using several kinds of solvent to control the dielectric constant, with increasing dielectric constant. Figure 1 also shows change in the specific surface area of the resultant nanoporous mullite ultrafine powders, prepared by using water as a excess solvent with increasing dielectric constant. These curves showed almost same tendency, suggesting that solid content in the precursor sols did not have considerable effect on the agglomeration behavior of the primary colloidal particles. From this figure, it is concluded that the important parameter, which determined the specific surface areas of the resultant nanoporous powders, is the dielectric constant of the solvent or agglomeration behavior. Namely, dielectric constant determined the thickness of electrical double layer on the ultra-fine primary particles and, therefore, relatively thin electrical double layer resulted in the coarse flock of the secondary particles in the sols. These coarse flocks of secondary particles have large pores and the capillary force during drying was not so large, leading to the nanoporous xerogel powders with coarse agglomeration state, if the solvents with low dielectric constants were used.

On the course of drying process, the large contraction in which fine wet gel powders lose solvent in the pores to form xerogel powders. This large shrinkage determines the

agglomeration state of the resultant xerogel powders and are strongly affected by the capillary force which arises from the evaporation of the solvent in the pores of the fine wet gel powders. This capillary force, ΔP, is described by the equation (2).

$$\Delta P = \frac{2 \gamma \cos \theta}{r} \qquad (2)$$
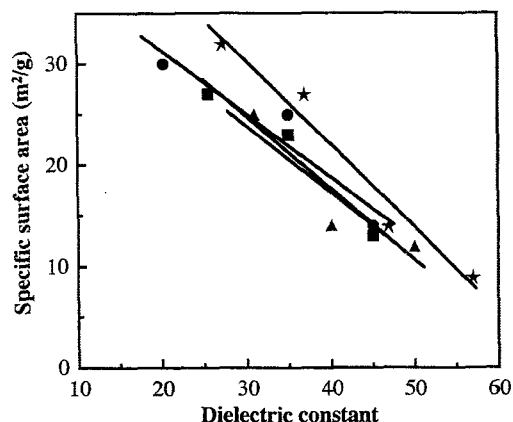

Fig.1 Relation between dielectric constants of solvents and specific surface areas of nanoporous mullite powders calcined at 1400 800 °C for 2 h. Precursor sols were prepared from different solvents by mixing water and various dielectric constant of ● ethanol, ■ acetone and ▲ acetonitrile, respectively. The concentration of the sols was fixed at 6.49 dm³/mol [TEOS].

From figure 1, specific surface area (SSA) of the nanoporous mullite powders is expressed by the following equation;

$$SSA = -0.68 \varepsilon + 44.41 \qquad (3)$$

where ε is the dielectric constant of the solvent used to prepare the precursor sols.

For the case of MDW, prepared slurry should be sprayed through the inkjet nozzle. Therefore, the prepared sols of nanoporous mullite precursor were spray-dried and calcined at 1400 °C.
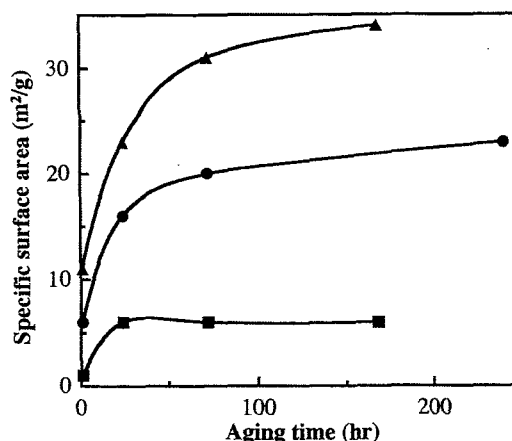

Fig.2 SSA of the nanoporous mullite ultrafine powders calcined at 1400 °C from different solvents.

Figure 2 exhibited the SSA of the calcined nanoporous mullite powders. It was demonstrated that the SSA of the nanoporous mullite also depended on the dielectric constant of the solvent even the nanoporous precursor powders were spray-dried. In addition, SSA of the calcined powders were leveled off for the aging after the hydrolysis, suggesting the agglomeration size of the primary nanoparticles would be limited in a sol. Figure 3 showed the pore-size distributions of the resulting nanoporous mullite from different solvents calcined at 1400 °C. The result of the pore-size distribution also supported the formation mechanism of nanoporous mullite powders and the pore size exhibited bimodal distribhution ascribed to the aggregation of primary particles and the agglomeration of secondary porous particles during spray-drying. Both pore sizes for the agglomerations were smaller in the case of the nanoporous mullite particles derived from i-butanol because of the lower dielectric constant of the solvent or thinner electrical double layer to enhance the aggregation in a sol.
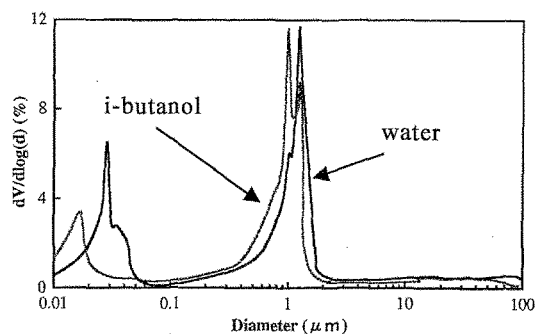

Fig.3 Pore-size distribution of the nanoporous mullite from different solvents of water and i-butanol, calcined at 1400 °C.

3.2 Slurry preparation and thin film deposition

In this study, nanoporous mullite powders were successfully prepared from molecular-designed precursor solution by controlling the coagulation behavior of the primary nanoparticles of mullite precursor. The final goal of this study is to prepare the suitable slurry of nanoporous oxide powders with low dielectric constant for MDW. For this purpose, we tried to prepare the slurries of nanoporous mullite precursor powders with low viscosity for easy sprying. Figures 4 and 5 exhibited the X-ray diffraction pattern and the changenin in the SSA for the nanoporous mullite precursor powders with calcining temperature, respectively. As already described, mullite precursor powders were amorphous as shown in figure 4 below 800 °C and exhibited very high SSA. In addition, amorphous mullite precursor is expected to be show low dielectric constant. Therefore in this study, nanoporous mulite precursor powder calcined at 800 °C was used to prepare the slurries for thin film deposition. At first, calcined precursor powder was pulverized to decrease the agglomerated secondary particle size by using the planetary mill. Figure 6 exhibited the change in
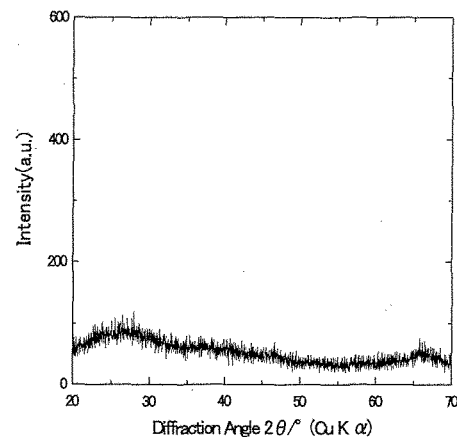

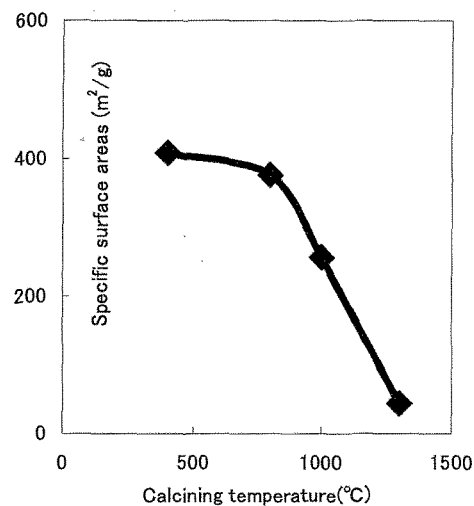Fig.4 XRD pattern for nanoporous mullite powder calcined at 800 °C for 2 h

Fig.5 Change in SSA for nanoporous mullite precursor powders with calcining temperature

the size distribution of nanoporous mullite precursor powders after milling for 2h at 400 rpm with aging for 24 h. The oxide concentration of each slurry was 1, 3 and 5 wt.%. All slurry exhibited relatively stable agglomeration behavior and showed small secondary particle size below 300 nm. Therefore, we tried to deposit thin films of nanoporous mullite precursor by spin-coating. Figure 7 showed the AFM images for the thin film surface deposited from slurries with different oxide concentrations. As a result, surface roughness of the deposited thin films increased with oxide concentration. However, the RMS value was not so large and exhibited relatively small RMS below 3 nm if the film was deposited from slurry with oxide concentration less than 3 wt.%.

Fig.7 AFM image for the surface of the nanoporous mullite thin film from slurry with oxide content of 3 %.
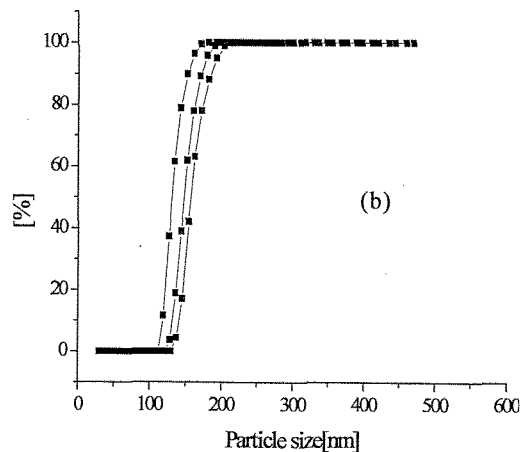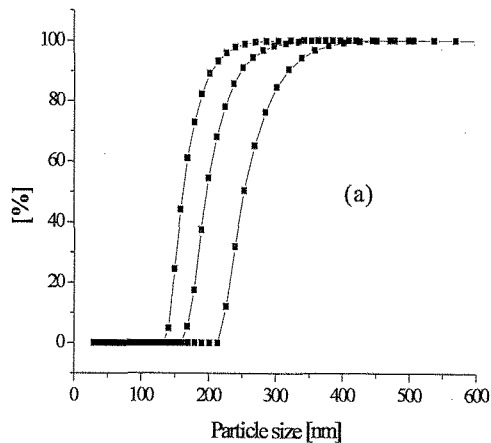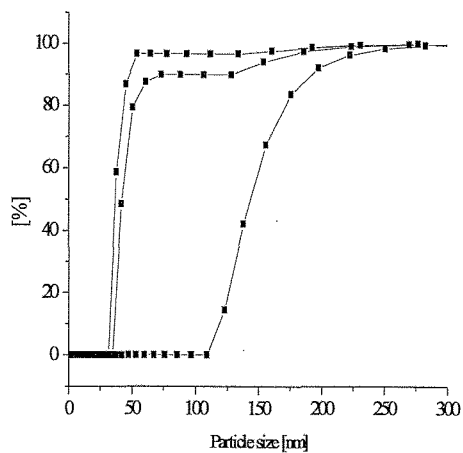

Fig.6 Size distribution of the agglomerated nanoporous mullite precursors in slurry with different oxide concentrations. (a) 1%, (b) 3%, (c) 5 %. Measurement has been done 3 times for all samples.
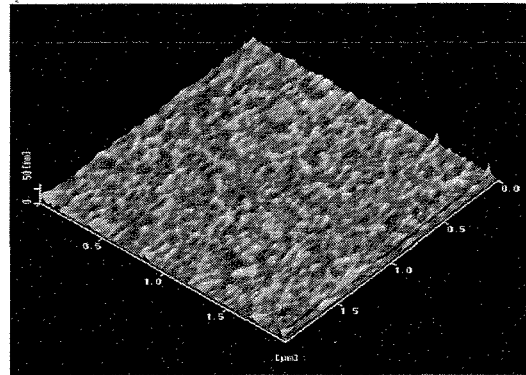
4. CONCLUSION

The agglomeration control for the wet chemical process is essential if the ultrafine powders were prepared. This paper described how to control the agglomeration state for the mullite precursor sol, and showed a novel processing for the porous mullite ceramic. As a result, it was concluded that thin electrical double layer of the sols in the solvents with low dielectric constant resulted in the coarsely aggregated flocks to form microporous mullite powders with very high surface areas even after high-temperature calcination, leading to the microporous mullite ceramic by gel-casting after sintering at 1400 °C.

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