

## Reinforcement of Porous Mullite Ceramics Using Ultra Fine Mullite Precursor Powders

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(Received September 23, 1998)

To increase the strength of high-purity porous mullite ceramics, ultra fine mullite precursor powders of about 10 nm in diameter were deposited at point of contact between primary coarse mullite particles of about 60  $\mu\text{m}$ . The deposited and hetero coagulated structures of ultra fine mullite precursor powders were controlled by pH. The optimum pH condition to form a uniform deposition of mullite powders between coarse mullite particles was in the range from 7 to 8. Deposition of the ultra fine powders did not form at  $\text{pH} < 7$  and  $\text{pH} > 10$  and irregular deposition was observed from  $\text{pH} 8$  to  $9$ .

**Key words :** Mullite, Zeta-potential, Hetero-coagulation, Permeability, Electrophoretic mobility

### I. Introduction

Porous ceramics have many industrial applications<sup>1,2</sup> such as filters, membranes, electronics and biomaterials.<sup>3</sup> The major requirements of filter materials for above application are high porosity, high mechanical strength and uniform pore size. However, it is difficult to fabricate the filters with high porosity and high strength by conventional methods, since an increase in porosity usually results in a decrease in strength. Mullite and cordierite porous ceramics have a high creep resistance and low thermal expansion coefficient. However, the densification of these ceramics need high temperature above the liquid formation temperature. The strength of ceramics with high porosity is generally low. One method to increase strength is to form a glass phase between particles by using a sintering aid, however, these glassy phase decrease the creep resistance.

In this paper, to increase the strength of high purity with porous mullite ceramics, high creep resistance, ultra-fine mullite precursor powders were hetero coagulated at point of contact between coarse mullite particles and hetero coagulated structure was controlled by pH. The optimum pH condition for deposition of mullite precursor particles at point of contact between coarse mullite particles is discussed.

### II. Experimental Procedure

#### 1. Approach

Fig. 1 shows the use of concentrated ultra-fine mullite

precursor powder at the contact point between coarse mullite to produce porous mullite ceramics. In this case, stoichiometric mullite precursor powders resulted from hetero coagulation and dispersion in suspension prior to drying. Uniform hetero coagulation structures in suspension were controlled by electrophoretic mobility distribution. Mullite precursor powders formed at point of contact between mullite particles pursuant to filter molding. Following this, mullite precursor powders reacted with mullite particles resulting in a high-purity porous mullite ceramic.

#### 2. Processing and characterization

The schematic for preparing uniform mullite precursor powder and porous mullite ceramic is given in Fig. 2. The particle diameter of the coarse mullite (Showa Denko, Ltd., Yokohama) used was 57.3  $\mu\text{m}$ . Commercial ultra-fine  $\gamma\text{-Al}_2\text{O}_3$  powder (TM-100, Taimei Chemical, Ltd., Nagano; specific surface area SSA, 134  $\text{m}^2/\text{g}$ ; estimated primary particle diameter  $d_p$ , 14 nm in diameter) was added to the alkoxide-derived  $\text{SiO}_2$  sol suspensions<sup>5</sup> and ball milling for 24 h. The molecular ratio of Al to Si was set at 3:2, corresponding to a stoichiometric mullite phase. Adding  $\text{HNO}_3$  solution gave uniform hetero-coagulation under a condition of  $\text{pH}=4.4$ .<sup>5,6</sup> Electrophoretic mobility distribution and zeta-potential of each particle was determined by a laser doppler method (Model, LZ-800, Otsuka, Ltd., Tokyo) at various pH, with hetero coagulates in suspension prepared by ball milling at  $\text{pH}=4.4$ . Coarse mullite particles were added to the uniform hetero-coagulated suspension and stirred for 1 h under conditions of  $\text{pH}=6$ ,

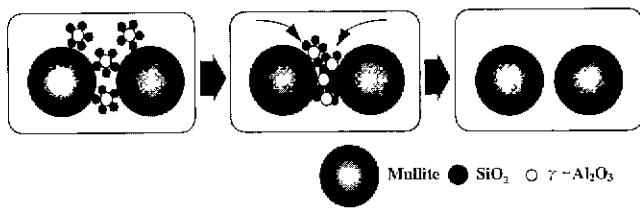


Fig. 1. Schematic illustration of reinforcement by concentration of ultra fine mullite precursor powders for the formation of porous mullite ceramics.

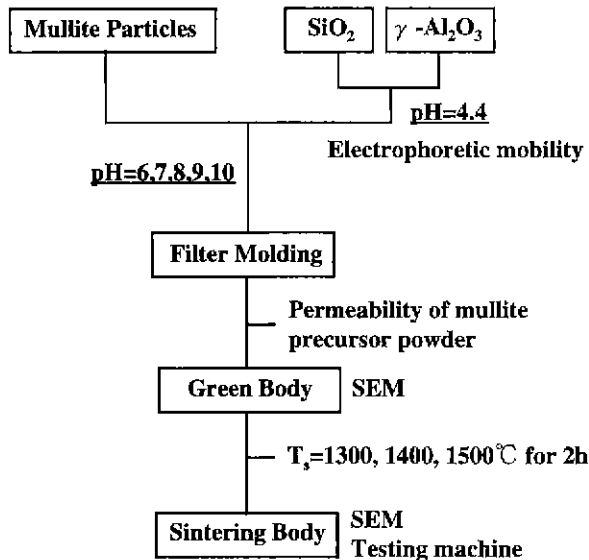


Fig. 2. Schematic diagram of the preparation of porous mullite ceramic and uniform mullite precursor powder by a colloidal process.

7, 8, 9 and 10. After stirring under various pH conditions, green bodies were prepared by filter molding from each suspension. The permeability of mullite precursor particles was calculated from the ratio of the total of original mullite precursor particles that passed particles through filter mold. The amount of total mullite precursor particles were the green body and the mullite precursor particles that passed through. The microstructure of green bodies produced by filter molding was observed with a scanning electron microscope (Model JSM-T100, JEOL, Ltd., Tokyo). Sintering was carried out in an electric furnace from 1300 to 1500°C for 2 h at a heating rate of 200°C/h. Microstructure of sintered bodies was observed with SEM. Furthermore, the fracture strength of sintered samples was measured at different sintering temperatures by a testing machine.

### III. Results and Discussion

To determine the optimum pH in suspension for hetero coagulation between coarse mullite particles and ultra-fine precursor particles, zeta-potential under varied pH conditions was investigated in suspensions by a laser

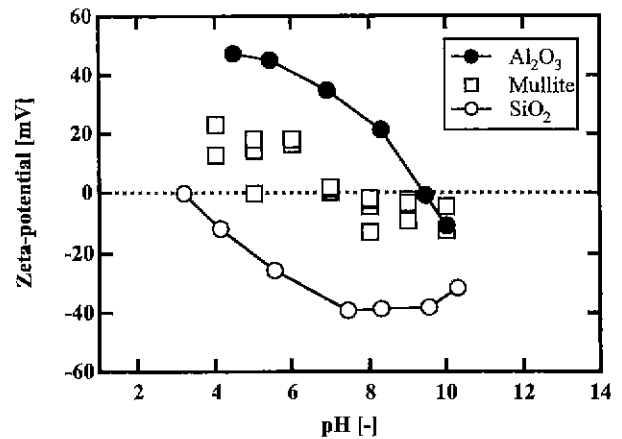


Fig. 3. Zeta-potential of alumina, silica and mullite particles.

doppler method. Fig. 3 shows the relationship between zeta potential for raw powders and pH in suspension. The isoelectric point of  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and mullite particles were pH=9, 3 and 7, respectively. Thus hetero-coagulation between  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and mullite particles was expected to occur in the range of pH=4~10.

Fig. 4 presents SEM micrographs of green bodies prepared by filter molding at pH=6, 7, 8 and 9 suspensions. In spite of counter charge condition between  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and mullite, deposition of mullite precursor particles between coarse mullite particles at a condition of (a) pH=6 was not observed. In cases of (b) pH=7, (c) pH=8 and (d) pH=9, deposition of mullite precursor particles was observed at the contact points between the mullite particles. However, deposition of mullite precursor particles to mullite particles formed not only at the contact point between mullite particles but also on their surface.

Fig. 5 shows the relationship between permeability of precursor powder during filter molding process and pH in suspension. The permeability of the precursor powder was about 100% under the condition of pH=6 since hetero-coagulates of precursor powder and coarse mullite particle did not occur. Almost all ultra fine mullite precursor powder passed between mullite particles and filter media during the filter molding process. The minimum permeability was obtained at pH=8, which precursor powder depositions was recognized almost all coarse mullite particles from the SEM observation result of the green body.

To determine the optimum and uniform hetero coagulation between  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  precursor powder and coarse mullite particle, electrophoretic mobility distribution of ultra-fine  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  particles in suspension prepared by ball-milling at pH=4.4 under various pH conditions was determined by a laser doppler method (Fig. 6). The arrows in Fig. 6 show the mode of electrophoretic mobility distribution of  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  particle suspension under each pH condition. Uniform hetero-coagulation between  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  was maintained below pH=7.1

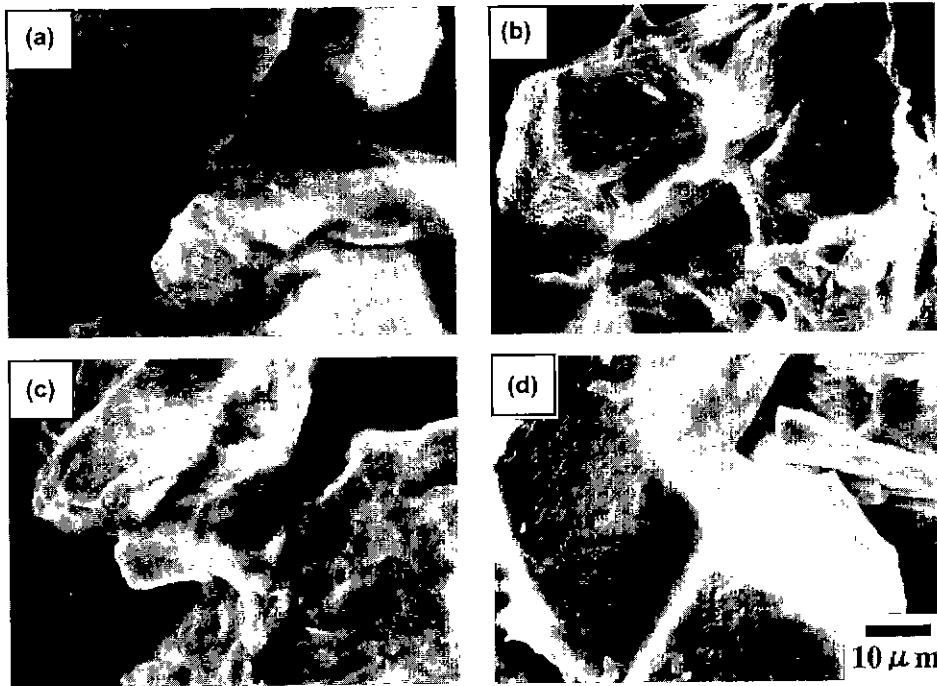


Fig. 4. SEM observations of microstructure after filter molding. (a) pH=6, (b) pH=7, (c) pH=8 and (d) pH=9.

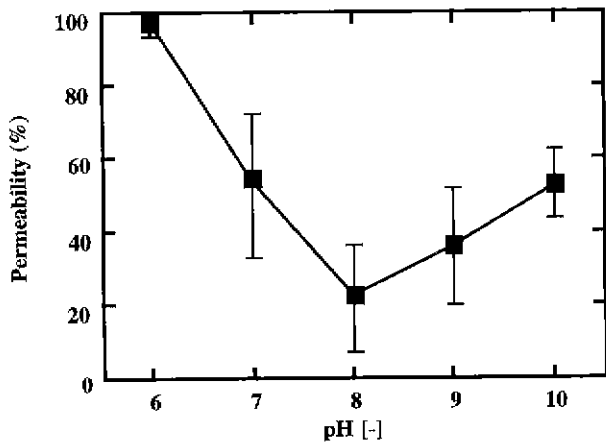


Fig. 5. Permeability of mullite precursor powder.

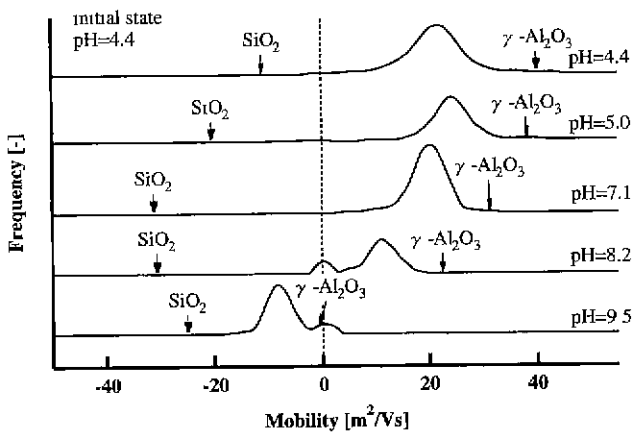


Fig. 6. Electrophoretic mobility distribution of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> suspension ball milled at pH=4.4 for 24 h.

since single-mode electrophoretic mobility distribution remained between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Bimodal distribution was observed in the range of pH  $\geq$  8.2. Accordingly, once uniform hetero-coagulation between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> formed during ball milling at pH=4.4, it retained a strong structure in a relatively high pH condition.

Fig. 7 shows schematic representations of hetero-coagulates between coarse mullite particles and ultra-fine mullite precursor powders under various pH conditions. This model is based on the result of SEM observation of green bodies prepared from filter molding, the permeability of mullite precursor particles and electrophoretic mobility distribution of each raw particle. Since the absolute value of position charge of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particle was larger than that of SiO<sub>2</sub> particle, hetero-coagulates of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> had a large positive charge, and can not deposition on coarse mullite particle due to electrostatic repulsion. On the other hand, at pH=7, which is almost isoelectric

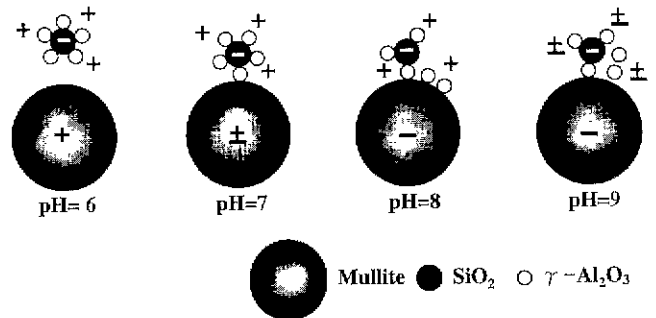


Fig. 7. Illustration of hetero-coagulation structure with different pH conditions.

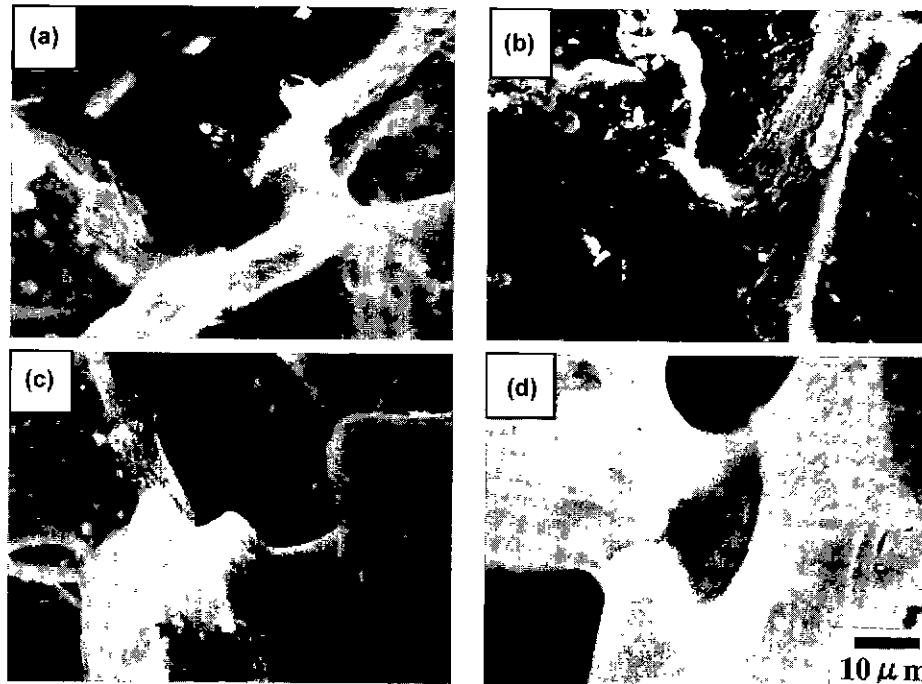


Fig. 8. SEM observations of porous mullite sintered at 1500°C for 2 h. (a) pH=7, (b) pH=8, (c) pH=9 and (d) pH=10.

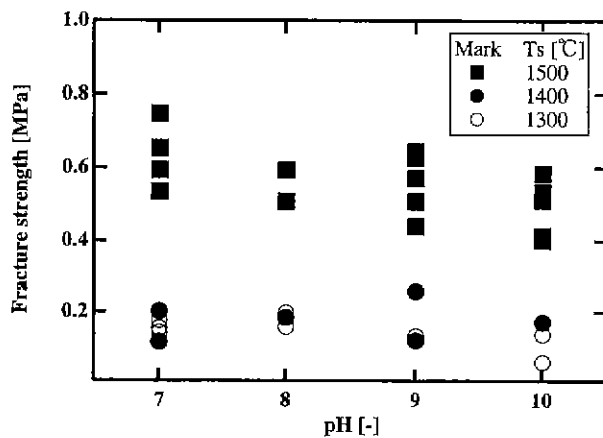


Fig. 9. Effect of pH on fracture strengths.

point of mullite particles, precursor and mullite particle can be formed weak hetero-coagulates without separation between  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2$  particles. Since separation between  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2$  took place at  $\text{pH} \geq 8$  (in Fig. 6), separated  $\gamma\text{-Al}_2\text{O}_3$  particles formed hetero coagulates on the surface of mullite particles and negative charged  $\text{SiO}_2$  particle at  $\text{pH} \geq 8$  can not deposit on mullite particle. The increase of permeability was occurred by the increase of free  $\text{SiO}_2$  particles in the range of  $\text{pH} > 8$ .

The microstructure of porous mullite ceramics sintered at 1500°C for 2 h is shown in Fig. 8. Owing to precursor powder deposition, a uniform and dense neck partly formed around the contact point of mullite crystal powder. The samples sintered at temperatures from 1300 to 1500°C for 2 h were offered for the measurement. The fracture strengths are shown in Fig. 9. Average fracture

strengths of all the samples are almost same strength until 1400°C. However, their fracture strength increases with increasing sintering temperature. The fracture strength increased on  $\text{pH}=7$  sintering temperature at 1500°C, which uniform precursor powder deposition was recognized (Fig. 6) and dense neck formed around the contact point of mullite crystal powder in Fig. 8(a). This result reflects that the stoichiometric deposition of ultra-fine powders as well as the condensation at point of contact between coarse mullite particle is very important for the increase the strength of high purity with porous mullite ceramics.

#### IV. Conclusion

The optimum pH condition existed for deposition of ultra-fine mullite precursor powders between the contact point of coarse mullite particles at  $\text{pH}=7, 8$ . Since precursor powders and coarse mullite particle have a same large positive charge at  $\text{pH} \leq 6$ . Almost all ultra-fine mullite precursor powders can not form hetero-coagulation and passed through between mullite particles under a  $\text{pH}=6$  filter molding condition. In instances of  $\text{pH}=7, 8$  and 9, deposition of mullite precursor particles was observed at the contact point between mullite particles. However, in the range of  $\text{pH} \geq 8$ , since the separation of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2$  particle due to electrostatic repulsion force, separated  $\gamma\text{-Al}_2\text{O}_3$  particles can formed hetero-coagulates on the surface of mullite particles.  $\text{SiO}_2$  particle pass through mullite powder layer and filter during filter molding process. In this condition, deposited ultra-fine powders can not keep stoichiometric conditions.

## References

1. J. F. Zievers, P. Eggerstede and E. C. Zievers, "Porous Ceramics for Gas Filtration," *Am. Ceram. Soc. Bull.*, **70**, 108-111 (1991).
2. K. K. Chan and A. M. Browsten, "Ceramic Membranes Growth Prospects and Opportunities," *Am. Ceram. Soc. Bull.*, **70**, 703-707 (1991).
3. W. A. Nancy, F. F. Lorraine and V. V. Bhaskar, "Macroporous Ceramics from Ceramic-Polymer Dispersion Methods," *AIChE Journal*, **43**(11), 2878-2888 (1997).
4. H. Kimiya, H. Suzuki, D. Kato and G. Jimbo, "Densification of Alkoxide-Derived Fine Silica Powder Compact by Ultra-High-Pressure Cold Isostatic Pressing," *J. Am. Ceram. Soc.*, **76**(1), 54-64 (1993).
5. Y. I. Cho, H. Kamiya, Y. Suzuki, M. Horio and H. Suzuki, "Mobility and Size Distribution Analyses of Hetero-Coagulated Structures of Colloidally Mixed Mullite Precursor Suspensions and their Sinterability," *J. Ceram. Soc. Jpn.*, **106**(2), 189-193 (1998).
6. Y. I. Cho, H. Kamiya, H. Takano, M. Horio and H. Suzuki, "Analysis of Hetero Coagulation Structure of Colloidal Mullite Precursor Powder -Experimental Approach and Computer Simulation-," *Mat. Res. Soc. Symp. Proc.*, **501**, 255-260 (1998).