

Fabrication of Mullite Powders by a Novel Processing**

By YueFeng Tang*, Liang Feng, YanFeng Chen, and AiDong Li

The ideal ceramic should be prepared from ceramic powders of tailored particle size and shape with no agglomerates, a narrow particle size distribution, high purity and high homogeneity. High homogeneity is very important especially in a system containing multicomponents. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the only intermediate stable compound in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ system and it is an important material for electronic, optical, and high-temperature structural applications,^[1,2] because of its superior electrical, thermal and physicochemical properties. Many methods have been used to prepare mullite powders,^[3-12] but the powders have been rarely prepared using heterogeneous nucleation and growth processing.^[5,6] Well characterized mullite powders are important for the preparation of mullite ceramics.

In this paper, a novel and general processing is proposed to solve the difficult problem of heterogeneity of the second constituent in the preparation of ceramics. Coating the second constituent on the cores is a good method to solve this problem. Heterogeneous nucleation and growth processing is the preferred coating process because it produces good control in the distribution of the second constituent. Using this process, sintering diffusion distance can be decreased, and mullite powders with no hard agglomerates and narrow particle size distribution were prepared from $\alpha\text{-Al}_2\text{O}_3$ and tetraethylorthosilicate (TEOS) as starting materials.

Fine particles can provide nucleation centers, and can decrease the kinetic barrier to nucleation of a supersaturated solution.^[13] In this experiment, $\alpha\text{-Al}_2\text{O}_3$ fine powders ($d_{50}=0.57 \mu\text{m}$) were used as nucleation centers in a supersaturated silica sol suspension.

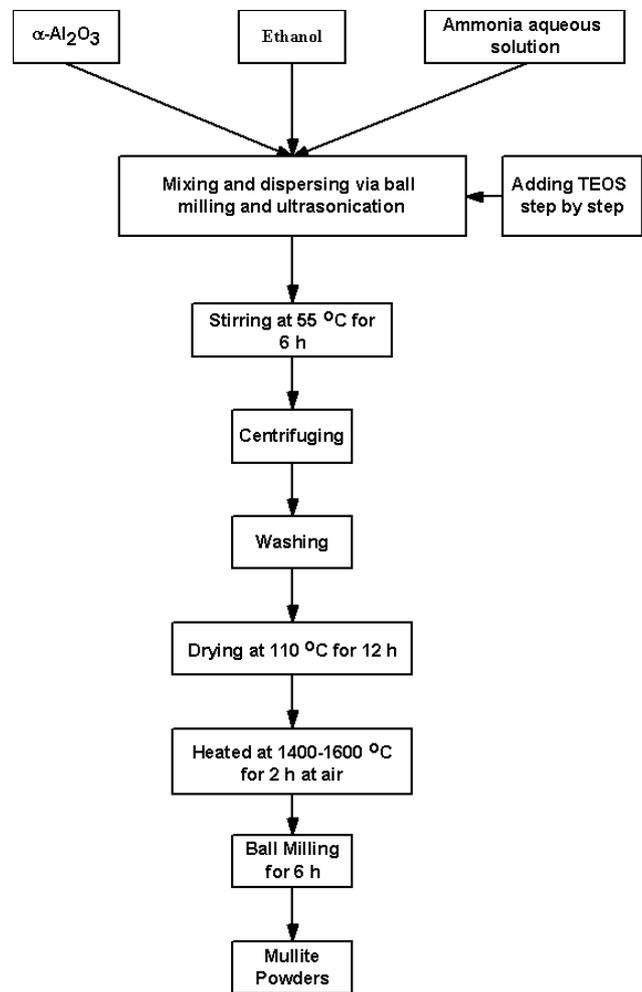


Fig. 1. The procedure of mullite powders.

The silica sol then forms a layer on the $\alpha\text{-Al}_2\text{O}_3$ cores by heterogeneous nucleation and growth processing. Fig. 2 shows the TEM micrograph of the composite coating particles. It was found that there was a layer on the $\alpha\text{-Al}_2\text{O}_3$ cores, and the thickness of layer was

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[**] This work is supported by a grant for State Key Program for Basic Research of China, the National "863" High Technology Program, National Natural Science Foundation of China (Contract No.: 50225204), Natural Science Foundation of Jiangsu province (Contract No.: BK2003071), Talents Training Foundation of Nanjing University and Pre-Study Natural Science Foundation of Nanjing University.

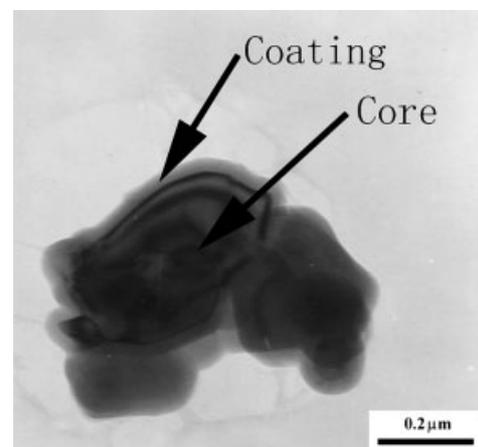


Fig. 2. TEM micrograph of composite coating particles

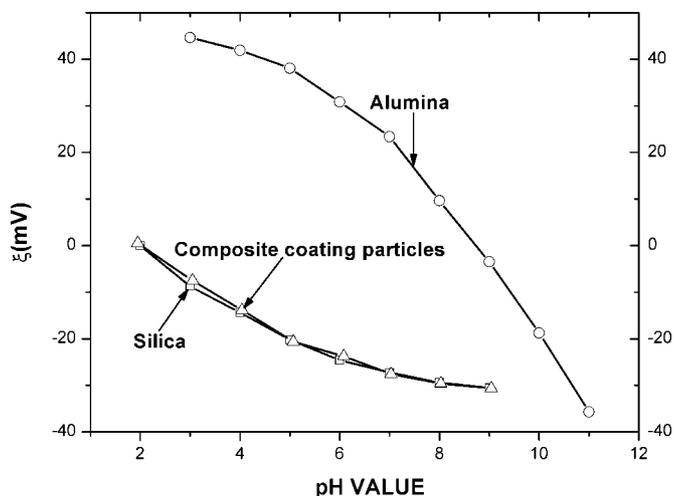


Fig. 3. Plots of the zeta potentials of silica, alumina and composite coating particles versus pH values (square is zeta potential of silica, triangle is zeta potential of composite coating particles, and circle is zeta potential of alumina)

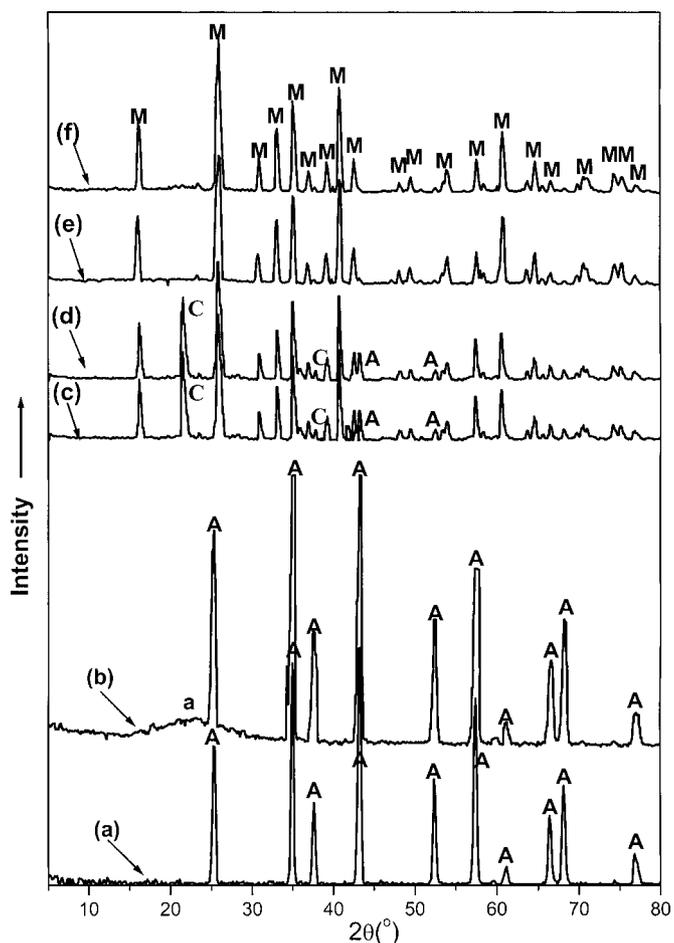


Fig. 4. XRD patterns of raw material (a) and composite coating particles (b) (a is amorphous silica, A is corundum), XRD patterns of composite coating particles calcined at different temperature (c) 1400 °C, (d) 1450 °C, (e) 1500 °C, (f) 1600 °C. (A is corundum, C is cristobalite, M is mullite)

about 25 nm. The alumina/silica ratio of the composite coating particles was controlled by the concentration of TEOS. The chemical analysis of the alumina/silica ratio of the particles was 74 wt%/26 wt%.

Comparing the XRD pattern of the α - Al_2O_3 raw material (Fig. 4a) with the XRD pattern of composite coating particles (Fig. 4b) shows that there was an expanding peak in the range of $2\theta \approx 22^\circ$. This is characteristic of amorphous silica. TEM observation (Fig. 2) also confirmed the presence of amorphous silica layer on α - Al_2O_3 cores.

Figure 3 shows the results of the zeta-potential measurement at different pH values. Comparing with zeta potential of silica and zeta potential of alumina, zeta potential of composite coating particles is similar to the zeta potential of silica, and it is different from the zeta potential of alumina. On basis of this fact, we think that silica sol has not self-nucleated to form silica powders. On the contrary, silica forms as a layer on the α - Al_2O_3 cores. Based on Fig. 2, it is confirmed again that α - Al_2O_3 cores are coated with a silica layer.

The phases of the composite coating particles changed when heated from 1400 °C to 1600 °C for 2 h (Fig. 4c–f). After the particles were calcined at 1400 °C or 1450 °C for 2 h (Fig. 4c,d), there were large amounts of mullite phase with small amounts of cristobalite and corundum. The single phase of mullite was obtained by calcining at 1500 °C for 2 h (Fig. 4e), and the peaks of the XRD pattern were sharpened with increasing temperature up to 1600 °C (Fig. 4f).

SEM observation showed that the mullite powders calcined at 1500 °C for 2 h after milling were composed of particles 0.2 to 1.0 μm in size (Fig. 5), and these mullite powders were not hard agglomerates. Fine mullite powders were easily obtained by ball milling. The particle size distribution analysis conducted on the powders gave a mean particle diameter (d_{50}) of 0.73 μm , and almost 80 % of the powders were finer than 1.6 μm as shown in Figure 6.

A novel and general processing (heterogeneous nucleation and growth processing) was found to solve the difficult problem of heterogeneity of the second constituent in the prepara-

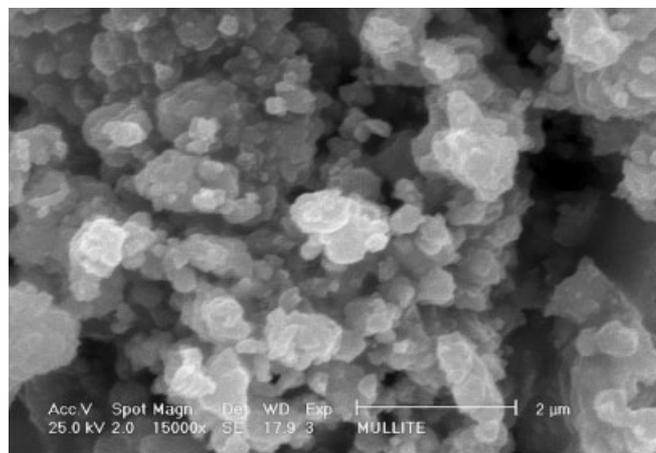


Fig. 5. SEM micrograph of mullite powders.

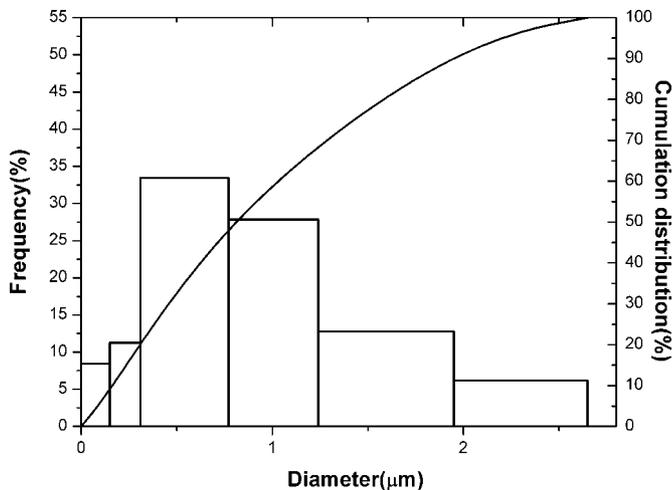


Fig. 6. Particle size histogram obtained by the sample shown in Fig. 5.

tion of ceramics. Composite coating particles of α - Al_2O_3 cores with an amorphous silica layer have been prepared by heterogeneous nucleation and growth processing. Phase pure mullite powders have been synthesized by calcinating at 1500°C for 2 h. Final powder after 6 h ball milling showed an average particle size (d_{50}) of $0.73\ \mu\text{m}$.

Experimental

Figure 1 shows the flow chart of the procedure used for the preparation of mullite powders. α - Al_2O_3 (average particle size (d_{50})= $0.57\ \mu\text{m}$) was dispersed in ethanol solution by ball milling for 2 h and ultrasonic homogenization for 10 min. The pH value of the suspension was adjusted to 11.5 by adding aqueous ammonia. TEOS was added step by step while the suspension was stirred at 55°C for 6 h. The alumina/silica ratio was adjusted to the mullite stoichiometric ratio by controlling TEOS concentration. Composite coating particles were collected by centrifuging, then washed with deionized water and dried in an oven at 110°C for 12 h. 50 g composite coating particles were calcined in air atmosphere between 1400 – 1600°C for 2 h at 50°C interval in a controlled electric furnace. The final products were ball-milled using alumina ceramic balls for 6 h to obtain fine powders.

The alumina/silica ratio, for the mullite powders prepared from the calcined composite coating particles, was obtained using chemical analysis (the potassium fluosilicate method). Phase analysis was performed on raw materials, composite coating particles and powders calcined at different temperatures by X-ray diffraction (XRD, Model Dmax/rb, Rigaku, Japan) using a nickel-filtered $\text{CuK}\alpha$ radiation. Transmission electron microscopy (TEM, Model STEM H-800, Hitachi, Japan) was used for microstructure observations. The zeta potentials of silica, alumina and composite coating particles were measured by Laser electrophoresis instrument (Lasser Zee, Model 500, USA). Scanning electron microscopy (SEM, Model XL 30, Philips, Holland) was used for microstructure observations of the calcined powders. Samples were sputter coated with a thin gold layer prior to the SEM observations. The particle size distribution analysis was conducted on the calcined particles by a laser particle size analyzer (Model MasterSize S, Marlvin, UK).

Received: September 19, 2003

- [1] I. A. Aksay, D. M. Dabbs, M. Sarikaya, *J. Am. Ceram. Soc.* **1991**, *74*, 2343.
- [2] K. Okada, N. Otsuka, S. Somiya, *Am. Ceram. Soc. Bull.* **1991**, *70*, 1633.
- [3] S. Somiya, Y. Hirata, *Am. Ceram. Soc. Bull.* **1991**, *70*, 1624.

- [4] M. Mineo, S. Hajime, *J. Am. Ceram. Soc.* **1991**, *72*, 377.
- [5] Y. F. Tang, A. D. Li, H. Q. Ling, Y. J. Wang, Q. Y. Shao, Y. N. Lü, Z. D. Ling, *Mater. Chem. and Phys.* **2002**, *75*, 301.
- [6] Y. F. Tang, A. D. Li, Y. N. Lu, X. Y. Li, S. Z. Shi, Z. D. Ling, *Appl. Surf. Sci.* **2002**, *202*, 211.
- [7] Jaymes Isabelle and Douy Andre, *J. Am. Ceram. Soc.* **1992**, *75*, 3154.
- [8] Hirata Yoshihiro, Sakeda Kazuyoshi, Matsushita Yumi, Shimada Kinji and Ishihara Yoshimi, *J. Am. Ceram. Soc.* **1989**, *72*, 995.
- [9] Ocana Manuel, Sanz Jesus, C. G. Teresita and J. S. Carlos, *J. Am. Ceram. Soc.* **1993**, *76*, 2081.
- [10] A. M. Katherine, C. III Joseph, M. S. Douglas and T. K. Toivo, *J. Am. Ceram. Soc.* **1992**, *75*, 213.
- [11] S. S. Satoshi and A. C. S. Cesar, *J. Eur. Ceram. Soc.* **1998**, *18*, 1145.
- [12] P. Murugavel, M. Kalaiselvam, M. K. Renganathan and A. R. Raju, *Mater. Chem. and Phys.* **1998**, *53*, 247.
- [13] N. B. Ming, *Physical Foundation of Crystal Growth*, China **1982**, Ch. 8.

Effectiveness of Surface Composite Layers on Impact Resistance of Brittle Materials

By Yeongseok Kim, Shijie Zhu, Yutaka Kagawa,* and Hideaki Kasano

Ceramic coatings have been used to protect surface of ceramics from environmental attack. However, the coatings are essentially brittle and not effective on mechanical damage.^[1–5] It is desirable that a ductile layer, like metals, is given on the surface because the layer would protect from the increase of stress in the bonded substrate.

The present authors evidenced the effectiveness of a thin damage-tolerant composite surface layer to prevent mechanical damages under quasi-static conditions.^[6,7] The major objective of the present study is to examine the potential of the surface composite layer to prevent impact damage on brittle materials.

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