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Paper

Particle Size Control and Characteristics Analysis of Nanosized γ-Alumina Powders

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Nanosized Al_2O_3 particles were synthesized using the thermal CVD (Chemical Vapor Deposition) method. $AlCl_3$ (Trichloroaluminum) was used as the starting material. The relationships between particle size and reaction temperature, and concentration and pressure were investigated. In the preparation of nanosized Al_2O_3 particles, the typical γ-Al_2O_3 crystalline phases appeared above 1273 K. The particle size decreases from 8.2 nm to 3.7 nm with reaction pressure in the range of 101 kPa to 42.5 kPa. We obtained the smallest average particle size of 3.7 nm with geometric standard deviation of 0.8 nm. TEM observation shows that particles are spherical in shape. The size was also found to decrease from 8.9 nm to 6.1 nm when the reaction temperature was increased from 873 to 1273 K in an $AlCl_3$ concentration of 0.014 mol%. The uniformity of Al_2O_3 particles increased and decreased $AlCl_3$ concentrations and reaction pressures. [Received August 6, 2003; Accepted December 19, 2003]

Key-words : Al_2O_3, Thermal CVD method, $AlCl_3$ (Trichloroaluminum)

1. Introduction

Nanosized powders have drawn considerable attention as raw materials of electrical parts and structural ceramics. Nanoscale particles of less than 0.01 μm in size have the unique properties of low sintering temperature and high activity catalsysis.[1)-4)] Nanoscale particles can be fabricated using the thermal evaporated condensation method by plasma or induction heater, laser ablation method, chemical vapor deposition (CVD) method, spray pyrolysis method, Sol-Gel method and milling process.[5)-7)] Recently, these manufacturing processes have been studied intensively to obtain the optimum manufacturing conditions and the synthesizing kinetics of nanosized powders. Among these processes, the CVD method is one of the most promising candidates due to the possibility of mass production of very pure nanosized powders with good size uniformity. In the CVD process, it has generally been recognized that the particle size is affected by various processing factors such as reaction temperature, gas species, pressure and precursor concentration. However, the influence of these factors on the synthesis has not yet been verified.

In this study, high purity nanosized γ-Al_2O_3 particles with homogeneous uniformity were synthesized using the thermal CVD method. The optimum conditions were obtained by varying the reaction parameters, i.e. reaction temperature, concentration and pressure. The size, shape and phase of the γ-Al_2O_3 particles were investigated under their various reaction conditions.

2. Experimental method

The nanosized γ-Al_2O_3 particles were prepared using the tube type thermal CVD system, which consisted of an evaporator, thermal reactor, filter and vacuum pump. **Figure 1** shows the schematic diagram of the thermal CVD system used in this experiment. $AlCl_3$ (Trichloroaluminum, TCA) as a raw material was evaporated in the evaporator and then carried into the reactor by He gas at a flow rate of 8.33×10^{-7} m^3/sec. The TCA concentration was changed from 0.014 mol% to 0.078 mol% by controlling the evaporation temperature under He atmosphere. Furthermore, a reactant gas such as $H_2O + O_2$ was delivered into the thermal reactor in order to react with the TCA. The flow rate of $H_2O + O_2$ gas was 1.66×10^{-5} m^3/sec. The reaction conditions were varied from 873 to 1273 K in temperature and from 42.5 kPa to 101 kPa in pressure. The synthesized γ-Al_2O_3 particles were collected in the attached micro-filters. The crystalline phases were identified by X-ray diffraction (XRD, RIGAKU RINT-2500) analysis using CuKα radiation. The particle morphologies and size were examined by transmission electron microscopy (TEM, HITACHI H-800) observation.

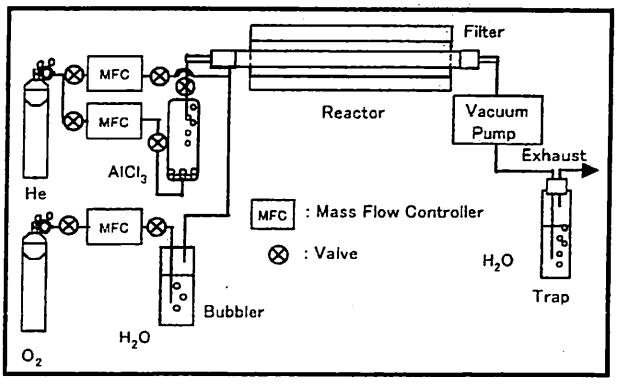

Fig. 1. Schematic diagram of the thermal CVD system.

3. Results and discussion

The phase change of synthesized Al_2O_3 particles showed dependence on reaction temperature. **Figure 2** shows X-ray diffraction patterns of Al_2O_3 particles for various reaction temperatures. The reaction temperature range was from 873 to 1273 K, and the TCA concentration was 0.014 mol%. XRD analysis shows that the crystalline phase of the particles was amorphous below 1173 K at atmospheric pressure. The typical γ-Al_2O_3 crystalline phases appeared at the reaction temperature above 1273 K. **Figure 3** shows a TEM micrograph of nanosized γ-Al_2O_3 powders synthesized at a reaction temperature of 1273 K. At that time, the TCA concentration was 0.014 mol%. The synthesized particles were spherical in shape. The average size was obtained by a logarithmic normal distribution method. The average particle size was 6.1 nm and geometric standard deviation was 1.1 nm. **Figure 4** shows the change in average γ-Al_2O_3 particle size as a function of reaction temperatures and TCA concentrations. When the reaction tempera-

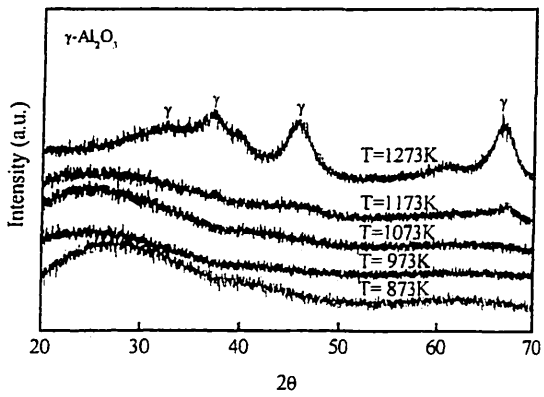

Fig. 2. The X-ray diffraction pattern of Al_2O_3 particles depends on reaction temperatures at a TCA concentration of 0.014(mol%).

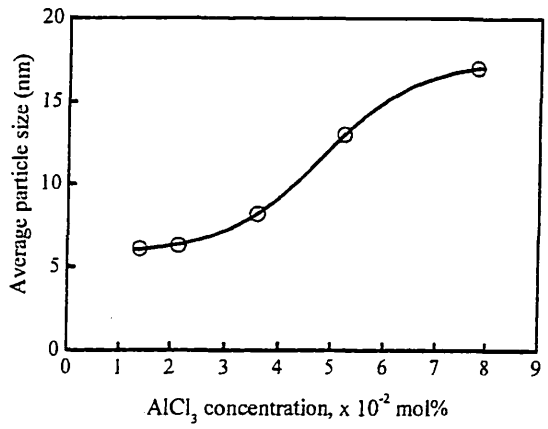

Fig. 5. Al_2O_3 average particle size as a function of TCA concentrations (mol%) at 1273 K.

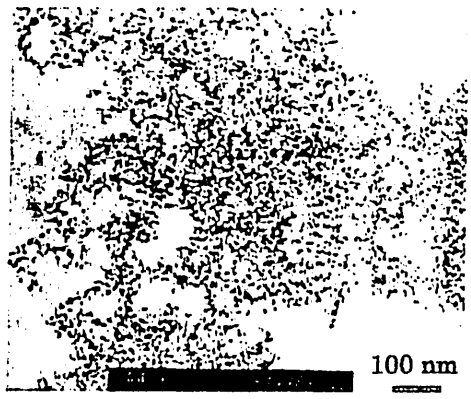

Fig. 3. TEM micrograph of γ-Al_2O_3 synthesized at a reaction temperature of 1273 K and TCA concentration of 0.014 mol%.

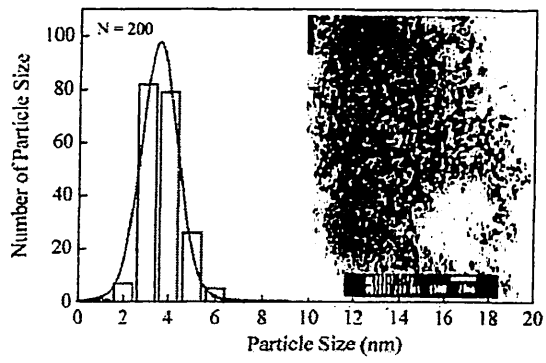

Fig. 6. The size distribution and TEM micrograph of Al_2O_3 particles synthesized at TCA concentration of 0.036 mol% and reaction pressure of 42.5 kPa.

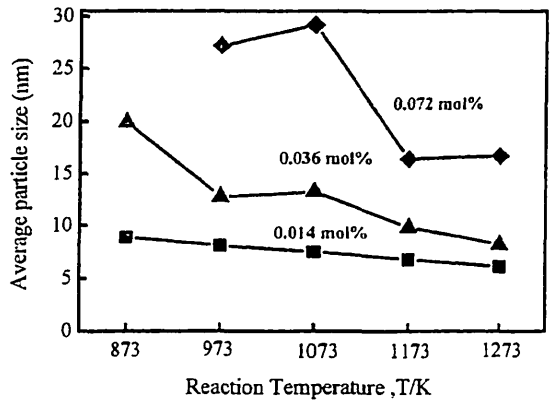

Fig. 4. Change of γ-Al_2O_3 average particle size as a function of reaction temperatures and TCA concentrations.

ture was increased from 873 to 1273 K at 0.014 mol%, the γ-Al_2O_3 particle size decreased from 8.9 nm to 6.1 nm. The Al_2O_3 particle size also decreases with decreasing TCA concentration.

The dependence of average γ-Al_2O_3 particle size on TCA concentration is shown in **Fig. 5**. The synthesizing temperature was 1273 K and TCA concentrations were changed from 0.014 to 0.078 mol%. In a TCA concentration of 0.014 mol%, the smallest average particle size (6.1 nm) was obtained. The average particle size decreased with decreasing TCA concentration. Moreover, it was observed that the particle size distributions have a narrow band with decreasing TCA concentration. The geometric standard deviation changed from 3.6 to 1.1 nm.

Figure 6 shows the size distribution and TEM micrograph of γ-Al_2O_3 particles synthesized at a TCA concentration of 0.036 mol% and reaction pressure of 42.5 kPa. It shows that the average γ-Al_2O_3 particle size and a geometric standard deviation are 3.7 nm and 0.8 nm, respectively. γ-Al_2O_3 particles synthesized under these conditions were obtained with high homogeneous uniformity. The dependence of average size of the γ-Al_2O_3 particles synthesized at 0.036 mol% at various pressures is shown in **Fig. 7**. In this study, the smallest average particle size of 3.7 nm was obtained at reaction pressure of 42.5 kPa. The particle size decreased from 8.2 to 3.7 nm with decreasing reaction pressures and the geometric standard deviation changed from 1.9 to 0.8 nm. The average size of γ-Al_2O_3 particles synthesized at 42.5 kPa was almost half of that at 101 kPa.

Nucleation of γ-Al_2O_3 powder occurred at the entrance of the reactor when the precursor was formed from the reaction between TCA and the reactant gas. The nuclei grow into particles when passed through the reactor. The particle size was determined by the number of nuclei in unit volume and the precursor concentration. It was observed that the number of nuclei existed in unit volume as the reaction decreases for

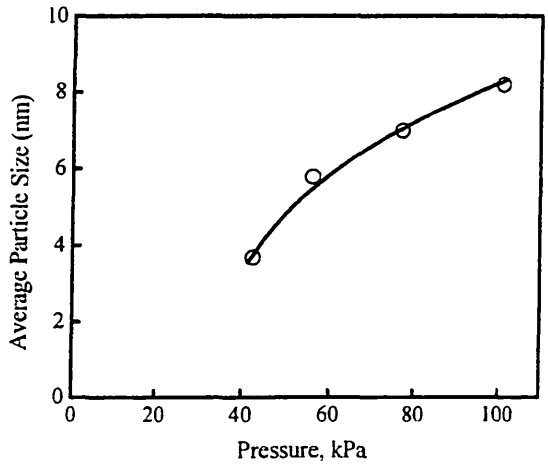

Fig. 7. The average particle size change of γ-Al_2O_3 powders synthesized at 0.036 mol% based on various pressure levels.

decreasing reaction temperature. From the above results, the nucleation occurred for a longer time than that performed at high temperature. As a result, the geometric standard deviation increased at low temperatures. When the same nucleus existed, concentration and pressure influence the particle size and the geometric standard deviation. At low concentration or low pressure, the nuclei have a few opportunities for collision within the precursor. Therefore, the particle size becomes smaller compared the case of high concentration or high pressure.

4. Conclusions

The effects of reaction temperatures, TCA concentrations, and pressures on the average particle size of nanosized γ-Al_2O_3 powders were investigated. The average particle size of the powders decreased when increasing the reaction temperature and decreasing the TCA concentrations or pressure levels. In the prepared nanosized Al_2O_3 particles, typical γ-Al_2O_3 crystalline phases appeared above 1273 K. We obtained the smallest average particle size of 3.7 nm with geometric standard deviation of 0.8 nm.

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