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Giant Alumina Particles Grown in Cluster Flux Produced by Cathodic Glow Discharge Coupled with He Gas Assisted Aggregation

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The giant particles of alumina have been generated by cathodic glow discharge coupled with helium gas assisted aggregation. The analyses of transmission electron microscope (TEM) images and electron diffraction patterns revealed some of the particles are tiny crystals of θ–alumina. The dependence of the particle size on the shape and the temperature of the source exit has been studied.

1. INTRODUCTION

Dispersed alumina fine particles have been widely used in industry as a support for various important catalysts. In such an application of alumina particles, it is desirable that the fine particles are uniformly distributed on a substrate without coalescence. Since the alumina particles are usually dispersed on a substrate by a wet process, it sometimes happens that the particles coalesce in sintering processes, which leads to reduction in effective surface areas. One of the solutions to this problem is to prepare alumina particles with narrow size distribution in gas phase and deposit them on a substrate.

For the practical use, an intense particle source is needed. Iijima has studied formation of alumina particles in the gas phase by a gas vaporization-aggregation technique[1-4]. Recently, Haberland et al. developed another type of particle source which involves cathodic glow discharge coupled with He gas aggregation[5]. One of the advantages of this source is that the size of the particles can be varied through a wide range.

In the present study we report formation of giant alumina particles in a similar cluster source employing the cathodic glow discharge. The analyses of transmission electron microscope (TEM) images and electron diffraction patterns revealed some of the particles are tiny crystals of θ–alumina. A time–of–flight (TOF) mass spectrometer and an atomic force microscope (AFM) have also been used to characterize the particles. The dependence of the particle size on the shape and the temperature of the source exit was examined.

2. EXPERIMENT

2.1 Cluster Source

The apparatus consists of a cluster chamber, a laser ionization chamber and a TOF mass spectrometer as shown in Fig.1. We have already described the latter two equipments in the previous paper [6]. The cluster source includes a magnetron sputtering gun which is located inside a cylinder made of stainless steel. To the top of the cylinder an aperture (2 mm diameter) or a stainless steel (SS) tube (4 cm long and 3 mm inner diameter) was attached to investigate the dependence of the particle size on the geometry of the source exit. The distance between the gun and the exit is 150 mm. The temperature dependence of the particle size was studied by cooling down the exit region by liquid nitrogen. The cylinder is filled with Ar (4×10^{-3} Torr) and He (10 Torr) gases, where Al atoms are sputtered off an aluminum target (5 cm diameter). Then, aluminum atoms aggregate in collision with surrounding He atoms. The function of He gas is not only to make the sputtered atoms aggregate but also to carry clusters from the source to the laser ionization chamber. The cylinder sits in the cluster chamber which is pumped down by a 5000 l/s oil diffusion pump. The base pressure in the cluster source was 2×10^{-6} Torr. The residual gas was dominantly water vapor.

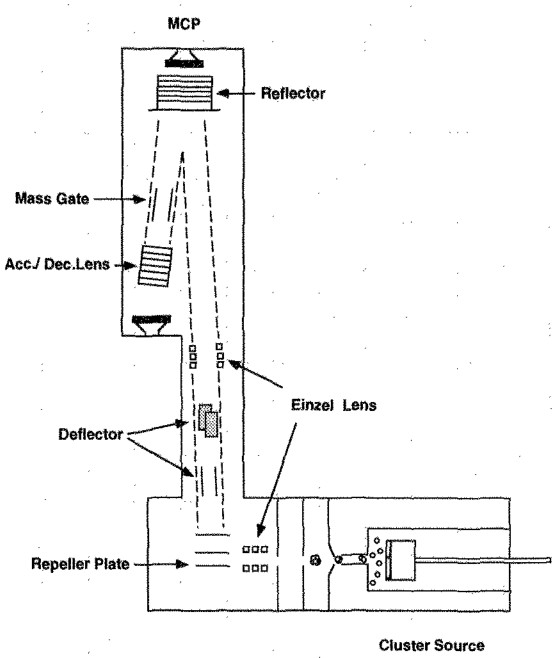

Fig.1 Schematic diagram of the apparatus.

2.2 Preparation of samples for TEM

For TEM observations, a copper mesh with micro grid carbon thin film was exposed to the particle flux for 30 min. The distance between the source exit and the mesh was 10 mm. Deposited particles were analyzed by a TEM operated at 100 kV or 200 kV (Hitachi HF-2000).

3. RESULTS AND DISCUSSION

3.1 Characterization of the giant particles by TEM

Fig.2 shows the TEM image of the generated giant particles. Particles were made in such a way that the SS tube was attached to the exit of the cylinder at room temperature. The diameters of most of the particles ranged from 70 nm to 100 nm. The image of one of the particles by the high resolution electron microscope is shown in Fig.3. The particle has a diameter of about 80 nm and a shape of truncated polyhedral. The plane spacing in the lattice image is 5.431 Å. We also found that the plane spacing of another particle was 2.026 Å. These agree quite well with the plane distance for θ-Al_2O_3 in which d_{100} = 5.45 Å, $d_{21\text{-}1}$ = 2.020 Å [7].

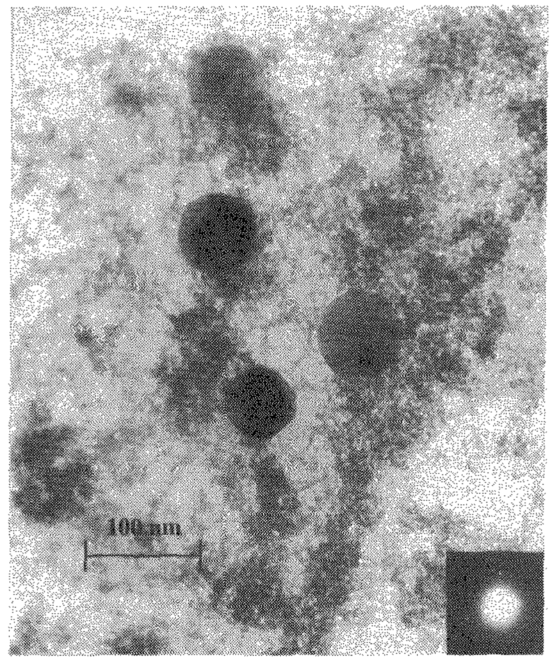

Fig.2 Giant alumina particles produced by cathodic glow discharge coupled with He gas aggregation.

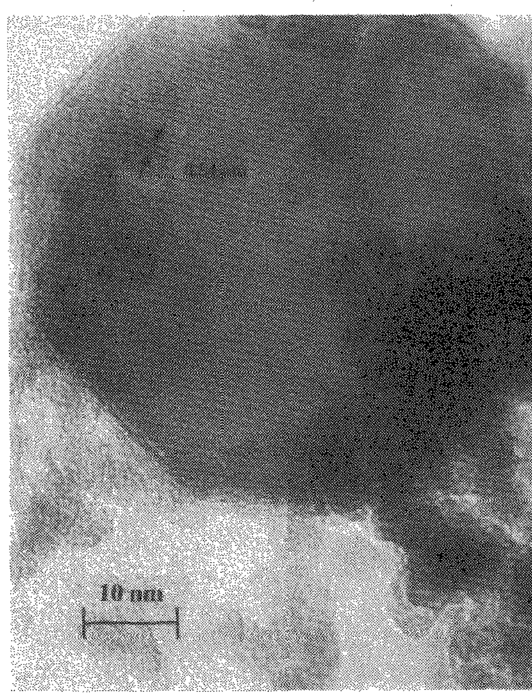

Fig.3 Image from the high resolution electron microscope of a giant alumina particle.

The electron diffraction pattern of these particles is shown in Fig.4. The analysis of these diffraction

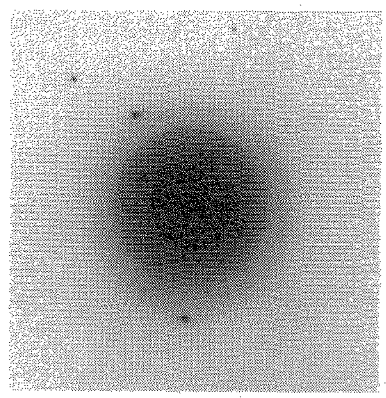

Fig.4 Electron diffraction pattern of the giant alumina particles.

spots shows that they can be explained as the diffraction from (222), (202), (217) planes of θ-Al_2O_3. From these results we conclude that the giant particles are tiny crystals of θ-Al_2O_3. As explained in the experimental section, there was a large amount of water in the residual gas. The observed θ-Al_2O_3 particles were probably produced by the reaction of aluminum atoms with the water molecules.

3.2 Size dependence of the alumina particles on experimental conditions

It is now well known in the field of cluster science that a shape and a temperature of a cluster source are important to determine the size of clusters. To investigate how these parameters affect the size of alumina fine particles generated in the present study, we prepared several samples under the following different experimental conditions and observed the particle size by TEM.

First, the alumina particles were generated without the SS tube and also without liquid nitrogen cooling. So, the alumina particles in the cylinder directly come out of the aperture of 2 mm diameter at room temperature. The TEM observation showed that the diameters of the alumina particles in this case were around 5 nm. Then, the SS tube is attached just behind the aperture without the cooling. It was found that the particles made with the tube have diameters of 50 to 200 nm. This result shows that the alumina particles generated in the cylinder make further collisions with one another and aggregate in the tube, resulting in the larger particles.

The exit region of the source was then cooled by liquid nitrogen to investigate the temperature effect. The TEM image revealed that the particle diameter is now reduced to 30–50 nm. This finding is consistent with that made by Haberland[5] and can be explained by a fundamental theory of nucleation.

An attempt was also made to observe particles existing in the vicinity of the Al target. This was done by inserting the SS tube close to the target to pick up the particles. Although a thin film was indeed made under this experimental condition, no TEM image of alumina particles was observed from the film. It is inferred that the particles from the region close to the target are too small to be observed by TEM.

3.3 Time of flight mass spectra

We have tried to measure the TOF mass spectra of positively charged particles in the flux. To increase the amount of positively charged particles, an OPO laser (230 nm) has been used to ionize the neutrals. The observed spectra are shown in Fig.5. The peaks in the time range from 13 to 22 μs were assigned to Al, AlO, Al_2 and Al_2O as shown in the figure. The observed species are probably due to photo-induced fragments from the parent alumina particles. The observation of the O-containing fragments supports the alumina particle formation in our source. For direct measurement of the particle

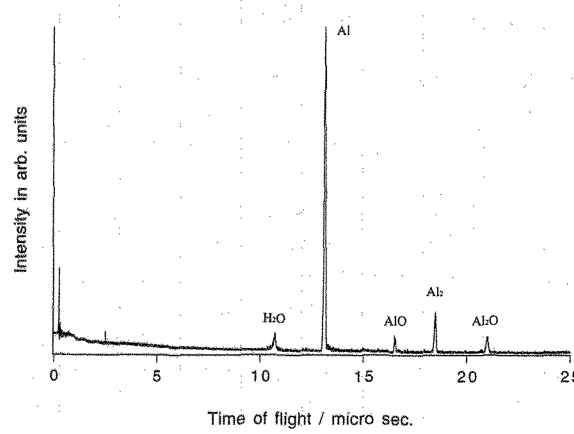

Fig.5 Time of flight mass spectra of fragment ions from alumina particles.

size distribution, a soft laser ionization without fragmentation is necessary, which is now underway in our laboratory.

4. SUMMARY

(a) Giant alumina particles have been generated by cathodic glow discharge coupled with He gas assisted aggregation.
(b) The analyses of TEM images and electron diffraction patterns revealed some of the particles have the structure of θ- Al_2O_3 crystal.
(c) The collimating tube at the exit of the source enlarges the alumina particles and thus works as a "particle growth tube". Cooling down the exit region of the source was found to reduce the particle size.

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