

## Properties and preparation of monodispersed spherical ultrafine particles by wet chemical process.

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**Abstract** Ultrafine silver monodispersed particles were prepared by wet chemical process. To decrease the reduction speed, an important factor in generating monodispersed particles, it is important to control three factors: synthesis temperature, concentration of aggregation-relaxing agent added, and concentration of silver nitrate solution. Synthesis of monodispersed spherical Ag particles used as metal powders for electrode became possible using the nucleus growth reaction method. In addition, control of the diameter of powder particles was also possible.

The silver particles distributed in narrow particles diameter with the averaged diameter of  $0.5 \mu\text{m}$ . TEM observation revealed that single crystalline silver particles were prepared by the present method.

**Key word:** monodispersed, single crystalline silver particles, spherical Ag particles

### 1. Introduction

Particles which have similar diameters and shapes are called monodispersed particles. A hydrolysis method using a metal alkoxide, so called the Stober type,<sup>1)</sup> has been studied as a synthesis method of monodispersed particles. Studies on monodispersed particles, mainly on ceramics particles such as titanium oxide ( $\text{TiO}_2$ ), zirconium oxide ( $\text{ZrO}_2$ ), tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) and titanate acid-lead zirconate (PZT), have been already performed, but research on metal powders for electrodes used in electronic ceramics is comparatively limited rare.<sup>2)-8)</sup> With respect to synthesis methods of metal powders used for electrodes, a wet synthesis method<sup>9)</sup> and a chemical vapor deposition (CVD) method<sup>10)-12)</sup> both of which involve a chemical reduction method, and an atomization-thermal decomposition method<sup>13)</sup> have been studied. Among these methods, vapor-phase methods such as CVD and an atomization-thermal decomposition method exhibit fairly good

monodispersing characteristics; however, with these methods, production cost is high, yield is low, and the particle-size distribution occurs over a wider range. In contrast, with the wet synthesis method, it is very difficult to synthesize monodispersed particles since the aggregating force is very strong; the number of reports on the synthesis of monodispersed particles using this method at both experimental and industrial levels is very few.<sup>8)</sup> With the increasing need for thinly layered internal electrodes and thin dielectric layers in miniature electronic equipment, the presence of aggregated particles, in addition to thin dielectric layers and thin internal electrodes, is becoming a significant cause of short circuiting between layers, wire breakage, and structural defects. Therefore, to avoid short-circuiting breakage between layers, use of independent, monodispersed spherical particles, which do not aggregate as do powder materials when used with dielectric layers and internal

electrodes, is essential.

In this study, we focused on the wet synthesis method using silver (Ag) metal microparticles which can be produced in large quantities at low cost, and which are often used as electrode material in the electronic ceramics field. We experimentally investigated the generation mechanism of Ag microparticles with the objective of synthesizing monodispersed spherical particles without aggregation.

## 2. Experimental method

In this study, we used a general wet synthesis apparatus and silver (Ag) as the subjective metal.

As a starting material, we used silver nitrate ( $\text{AgNO}_3$ ) containing 63.5% Ag, which is solid at room temperature and is generally used for industrial purposes. First, the silver nitrate was dissolved in purified water to obtain a silver nitrate solution. Gum arabic was then added to relax particle aggregation. The silver nitrate solution was then reduced using hydrazine ( $\text{N}_2\text{H}_4$ ) and silver particle were obtained. Table 1 shows synthesis conditions of this experiment.

The dispersion characteristics of the synthesized silver particles were evaluated using a microtrack particle-size laser analyzer (Nikkiso Co., Ltd.HRA 100 TYPE). The microstructure of the synthesized particle surfaces was observed using a scanning electron microscope (SEM). Crystallinity of the particles was evaluated by electron beam diffraction measurements, as well as by the observation of the internal structure using a transmission electron microscope (TEM). Crystal sizes were obtained by X-ray diffraction (XRD) measurements. Fine-particle characteristics of the obtained silver particles were evaluated by measuring tap-density, and the specific surface area was obtained by the (BET) method.

Table 1. Synthesis Condition of Ag Powders

	(a)	(b)	(c)
$\text{AgNO}_3$ concentration(g/l)	80	4~80	2
Synthesize temperature( $^{\circ}\text{C}$ )	-10~30	5	5
Gum arabic concentration(g/l)	3.75	3.75~11.25	7.5
$\text{NaOH}$ concentration(g/l)	24	—	—
$\text{N}_2\text{H}_4$ concentration(g/l)	—	27.2	27.2

## 3. Experimental results and discussion

### 3.1 Synthesis of monodispersed particles

#### 3.1.1 Effects of synthesis temperature on synthesis of Ag particles

The effects of synthesis temperature on generated Ag particles were investigated using their precursor, silver oxide ( $\text{Ag}_2\text{O}$ ); the reason for this is as follows. Since the reduction rate was high under the concentrations set in this experiment, Ag particles aggregated extensively; therefore, it is difficult to assume that the shapes of the reduced Ag particles were observed. In addition, according to Hamada et al.,<sup>14)</sup> there is a certain relationship between the shape and the diameter of the oxidized and reduced particles.

Table 1(a) lists detailed synthesis conditions; 80g/l silver nitrate solution, 3.75 g/l gum arabic solution as a aggregation-relaxing agent, and 24 g/l sodium hydroxide (caustic soda) were used under synthesis temperatures between  $-10^{\circ}\text{C}$  and  $30^{\circ}\text{C}$ . The effects of synthesis temperature on the generated  $\text{Ag}_2\text{O}$  particles were investigated.

Figure 1 shows scanning electron micrographs and particle-size distribution of  $\text{Ag}_2\text{O}$  particles obtained at different temperatures. As the synthesis temperature decreases,  $\text{Ag}_2\text{O}$  particle size tends to increase, and as the synthesis temperature increases,  $\text{Ag}_2\text{O}$  particle size tends to decrease; the reason for these phenomena can be explained as follows. For the former, since the speed of silver nitrate oxidation by sodium hydroxide decreases with decreasing synthesis temperature, the number of  $\text{Ag}_2\text{O}$  nuclei decreases; as a result, generated  $\text{Ag}_2\text{O}$  particles tend to be used for deposition and growth of the nuclei of silver particles. In contrast, regarding the latter phenomenon, an increase in the synthesis temperature increases the oxidation rate which results in an increase in the number of  $\text{Ag}_2\text{O}$  nuclei; accordingly, the amount of  $\text{Ag}_2\text{O}$  used for deposition and growth of the nuclei of  $\text{Ag}_2\text{O}$  particles decreases. As a result, the size of synthesized  $\text{Ag}_2\text{O}$  particles decreases.

As the results from measuring particle-size distribution show (Fig. 1), the distribution range is separated into two regions as the synthesis temperature decreases. In this figure, the frequency peak appearing on the coarse-particle side (a) is due to nuclei growth. Conversely, the frequency peak appearing on the fine-particle side (b) is due to particle

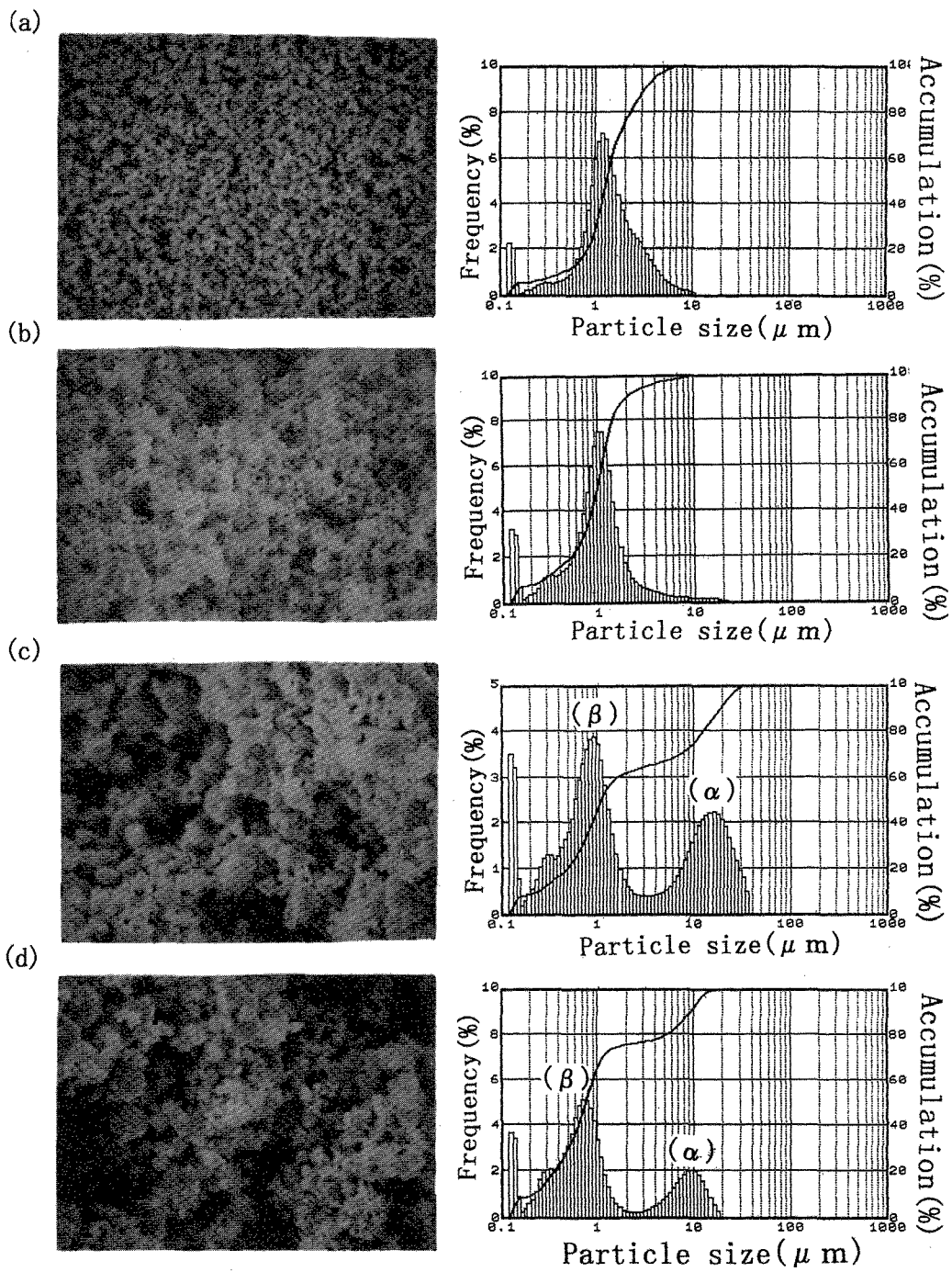


Fig. 1. SEM photograph and a particle size distribution measured by Microtrac laser particle size analyzer with various synthesis temperature.  
 (a) 30°C, (b) 10°C, (c) 0°C, (d) -10°C.

growth of new  $\text{Ag}_2\text{O}$  nuclei stemming from the remaining silver nitrate. Therefore, in the particle-size distribution when the synthesis temperature is  $0^\circ\text{C}$  or  $-10^\circ\text{C}$  (low temperature), the two types of  $\text{Ag}_2\text{O}$  particles that are generated from two mechanisms, nucleation and particle growth, are considered to be mixed.

### 3.1.2 Effects of aggregation-relaxing agent on synthesis of Ag particles

We investigated the effects of gum arabic, which was added to relax Ag particle aggregation during reduction, on the generation of Ag particles. Table 1(b) shows detailed experimental conditions; 80 g/l silver nitrate solution and 27.2 g/l hydrazine (reducing agent) were used with varying amounts of gum arabic, in a range between 3.75 - 11.25 g/l, under a constant synthesis temperature of  $5^\circ\text{C}$ . Figure 2 shows particle-size distribution of

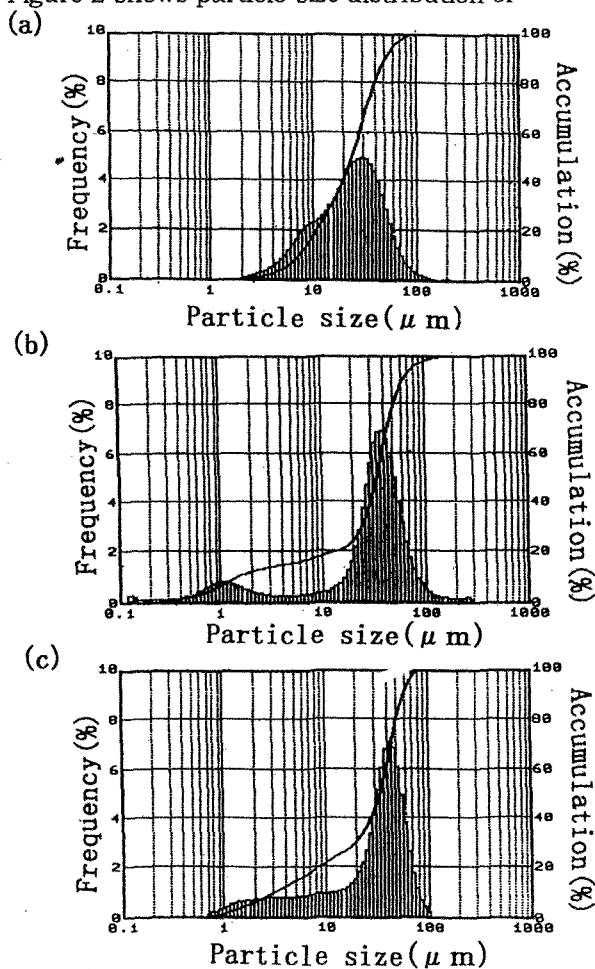


Fig. 2. A particle size distribution measured by Microtrac laser particle size analyzer with various gum arabic concentration. (a) 3.75 g/l, (b) 7.5 g/l, (c) 11.25 g/l.

generated Ag particles when various amounts of gum arabic are added. By increasing the amount of gum arabic, the distribution range of the particle size narrowed and the monodispersion characteristics improved.

The average primary Ag particle size was 30  $\mu\text{m}$ , which did not change with the amount of gum arabic added. Furthermore, addition of an excessive amount of gum arabic significantly delayed the Ag particle sedimentation separation from the water phase, making it extremely difficult to remove the Ag particles as dried powders. Therefore, in subsequent experiments, the amount of gum arabic added was set at 7.5 g/l, the limit at which successful sedimentation separation could occur.

### 3.1.3 Effects of the concentration of silver nitrate on the synthesis of Ag particles

When Ag particles are generated using the wet synthesis method, the most important factor is considered to be the concentration of silver nitrate solution during synthesis. We investigated the effects of this factor on the size and aggregation of Ag particles.

Synthesis conditions were as follows (Table 1(b)). Synthesis temperature was set constant at  $5^\circ\text{C}$ , the amounts of gum arabic added and hydrazine (reducing agent) were set constant at 7.5 g/l and 27.2 g/l, respectively, and the concentration of silver nitrate was varied between 4 - 40 g/l.

Figure 3 shows scanning electron micrographs and particle-size distribution of generated Ag particles. As the concentration of silver nitrate solution decreases from 40 g/l to 4 g/l, the particle size decreases and the number of aggregated particles decreases, showing uniform particle size distribution.

### 3.2 Nucleation and growth mechanism of Ag particles

We investigated the synthesis temperature, the amount of aggregation-relaxing agent, and concentration of silver nitrate solution as the three major factors involved in obtaining monodispersed particles using the wet synthesis method. The results demonstrated that the reduction rate is closely related to the synthesis of monodispersed particles, and that it is important to decrease the concentration of the silver nitrate solution under low synthesis temperatures while adding the proper amount of aggregation-relaxing agent.

Referring to the above experimental results and

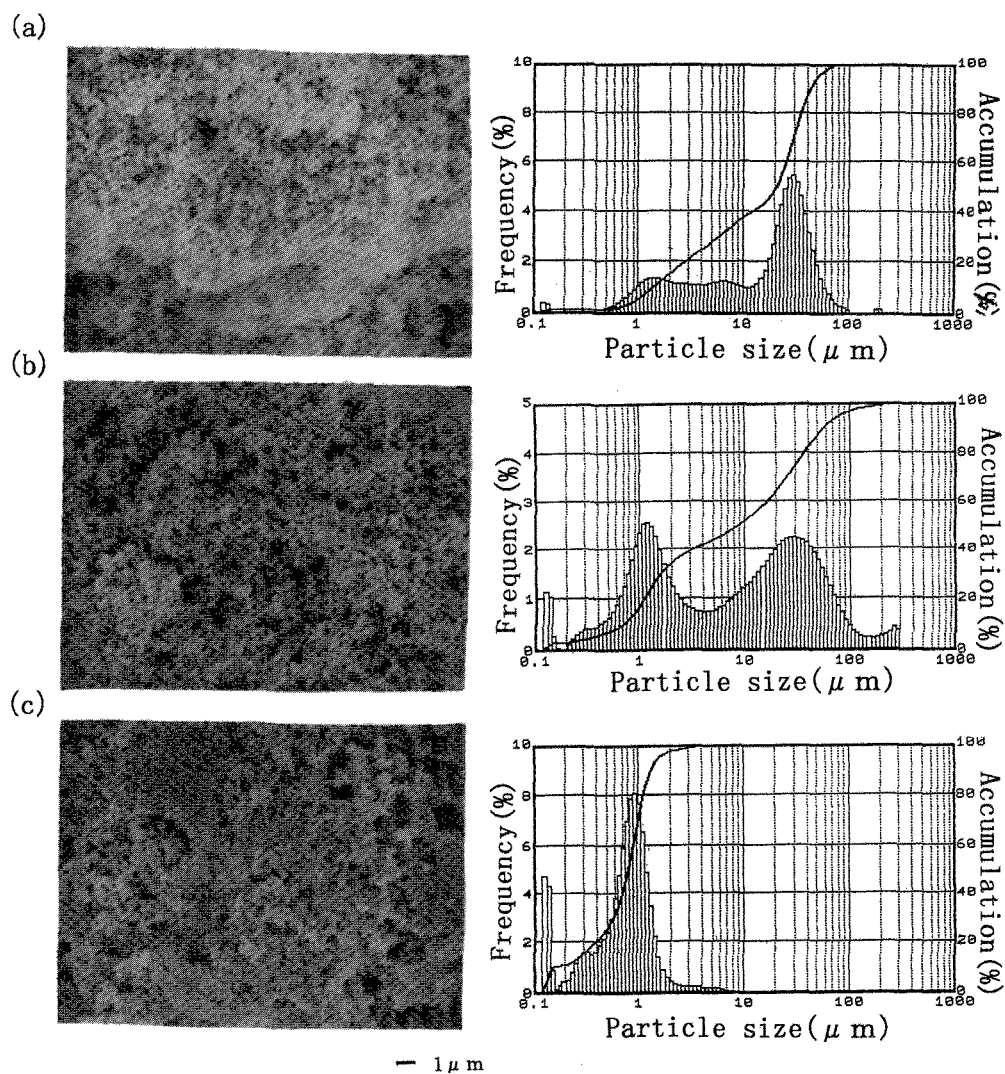


Fig. 3. SEM photograph and a particle size distribution measured by Microtrac laser particle size analyzer with various AgNO<sub>3</sub> concentration. (a) 40 g/l, (b) 20 g/l, (c) 4 g/l.

based on the basic idea of the generation method of monodispersed particles reported by LaMer,<sup>15)</sup> we discuss "the synthesis method of independent monodispersed spherical Ag particles using a 2-step growth method," which consists of nucleation of Ag in a low-concentration silver nitrate solution, and the growth of Ag particles from the generated nuclei.

Figure 4 shows schematics of generation and growth of particles reported by LaMer. When a small amount of solute is added at a time, the concentration of the solute increases at once; however, a reduction reaction occurs simultaneously with the addition, resulting in the gradual decrease in the solute concentration following its local maximum value that quickly occurs prior to the reduction

reaction, and the solution finally reaches its supersaturation concentration. This process can be divided into three regions. When a solute is continuously added to a reaction system, solute concentration increases instantly; when the solute concentration exceeds its equilibrium solubility,  $C_s$ , the solute concentration in the reaction system becomes supersaturated since the solute can no longer be dissolved (region I). Next, when the solute concentration is further increased, nucleation begins at  $C_{min}$ ; since the solute is rapidly consumed by nucleation, the increase in the solute concentration is terminated and the solute concentration becomes a maximum solute concentration,  $C_{max}$ , at a point where supply and consumption of the solute become equal (region II). If the solute is no longer added when nucleation begins, the solute concentration drops immediately, and further nucleation is terminated since the supersaturation concentration decreases (region III). The size limit of the nuclei is said to be defined by a bonding of 30-50 molecules with solubility-resistant bases; therefore, the size of the synthesized nucleus is likely to be approximately 1 nm.

In this experiment, based on the above-mentioned nucleation and particle growth mechanisms, we applied the synthesis conditions shown in Table 1(c).

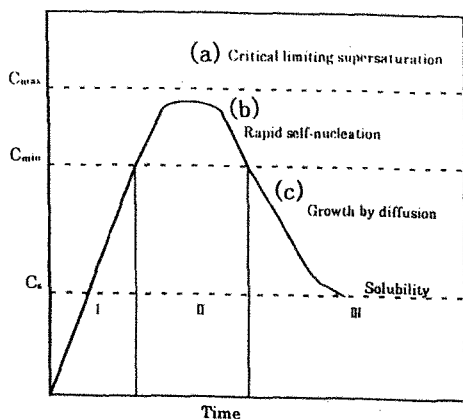


Fig. 4. LaMer's model for the formation of a homodispersed system by controlled homogeneous nucleation and growth. I: Prenucleation period, II: Nucleation step, III: Growth step.

Figure 5 shows scanning electron micrographs of particles at each step during their growth, starting from nucleation. As the micrographs

clearly show, the average diameter of the nuclei which began to grow early changed from 0.1  $\mu\text{m}$  to 0.5  $\mu\text{m}$  by the time growth ceased. In addition, the Ag particles which grew to be 0.5  $\mu\text{m}$  in diameter became independent monodispersed spherical particles and did not aggregate.

Using the above results, we calculated the final growth efficiency, i.e., the ratio of the amount of Ag added for particle growth from the amount of total Ag added.

First, diameters of the generated nuclei were obtained from a scanning electron micrograph, and the weight of one nucleus was calculated using eq. (1).

The weight of a nucleus (A) = volume of the sphere (V) x specific gravity (d) eq. (1)

A number of nuclei (C) can be calculated from eq. (2) below, using the weight of the added Ag (B).

$$C = B/Aeq \quad \text{eq. (2)}$$

Similarly, the diameters of the grown Ag particles were obtained from a scanning electron micrograph, and the weight of one Ag particle was calculated using its volume and true density. The number of grown Ag particles was estimated from an inverse calculation using the weight of the added Ag. The weight of Ag consumed in order to grow Ag particles (E) was obtained using eq. (3) below.

$E = (\text{volume of a grown particle} - \text{volume of a nucleus}) \times \text{specific gravity of Ag} = \text{volume of a grown particle} \times \text{specific gravity of Ag}$  eq. (3)

Accordingly, the total weight of Ag consumed to synthesize Ag particles (F) can be given by eq. (4) below.

$F = (\text{weight of one grown Ag particle} (E) \times \text{number of grown Ag particles})$  eq. (4)

The final growth efficiency (G) which is the ratio of the amount of Ag added for particle growth from the amount of total Ag added can be calculated using eq. (5) below.

$G = \text{weight of grown Ag particles} / \text{weight of Ag added}$  eq. (5)

Using these equations, the final growth efficiency under the experimental condition (b) in this study was calculated to be 87.4%. Thus, most of the Ag added was considered to be consumed enabling nuclei growth, whereas the remaining 12.6% of the Ag added was used for new nucleation. More detailed studies on these phenomena are required in the future.

Figure 6 shows results of the investigation of the relationship between the amount of Ag

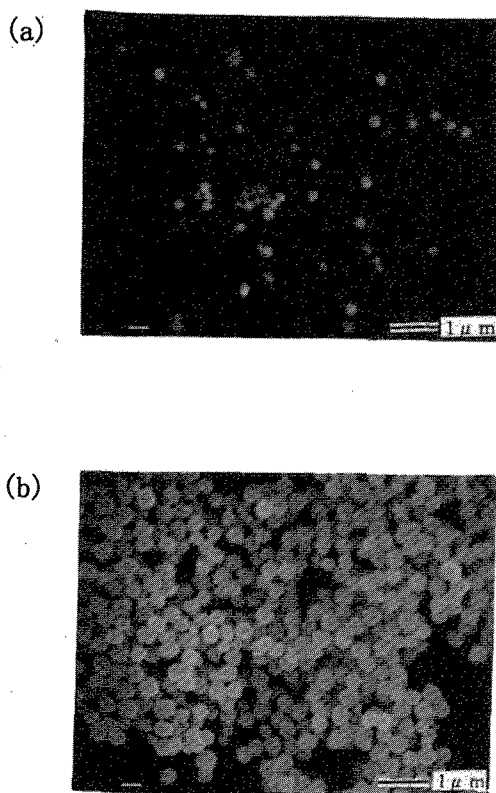


Fig. 5. SEM photograph of nuclear silver particle and grown up silver particle. (a) Nuclear silver particle, (b) grown up silver particle.

added and particle diameter (particle growth) using SEM.

The results indicate that particle diameter can be controlled by regulating the amount of Ag added.

Powdered particles collected from a slurry usually become, as is well known, aggregated particles. These aggregated particles may initially be independent monodispersed particles in the slurry, however, they may be reaggregated during collection from the water phase and dried to obtain powders.

Therefore, we investigated the occurrence and advancement of reaggregation from the slurry state to the dried powder state. We directly measured the particle-size distribution of the slurry, and compared the results with the particle-size distribution of the dried powder obtained from this slurry. In addition, we added an organic self-tissue-membrane-forming agent to another slurry, and obtained powder from this slurry by drying. Particle-size distribution was then measured in order to examine the aggregation advancement.

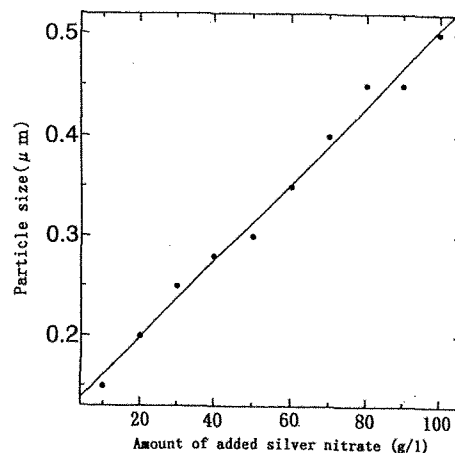


Fig. 6. Relationship between amount of added silver nitrate and particle diameter.

As a result, the particle-size distribution of the powders collected from the slurry in which the organic self-tissue-membrane-forming agent was added was almost identical to that obtained from the direct measurement of the slurry; however, that of the dried powder collected from the slurry with no added agent contains significantly coarser (large) particles. These results indicate that use of the organic self-tissue-membrane-forming agent can suppress particle reaggregation during drying. Figure 7 shows transmission electron micrographs and electron-beam diffraction spots of synthesized Ag particles using a nucleation-reaction method. The Ag particles synthesized show a hexagonal shape indicating high crystallinity, and consist of monocrystals, as indicated by the apparent electron-beam diffraction spots.

The following two mechanisms are proposed as the likely generation mechanism of monocrystal-like particles. (1) According to the crystal growth mechanism proposed by Mizutani et al.,<sup>16)</sup> solute molecules are adsorbed to terraces and kinks of spiral transition, are transferred by surface dispersion and incorporated into crystals.

(2) Matijevic et al.<sup>17)</sup> proposed that solute molecules were adsorbed onto the entire surface of the nuclei, resulting in the occurrence of two-dimensional multinuclei-layer growth on the surface. With respect to the nuclei generated in our experiments, it is difficult to consider the occurrence of the transition proposed in (1); the generation



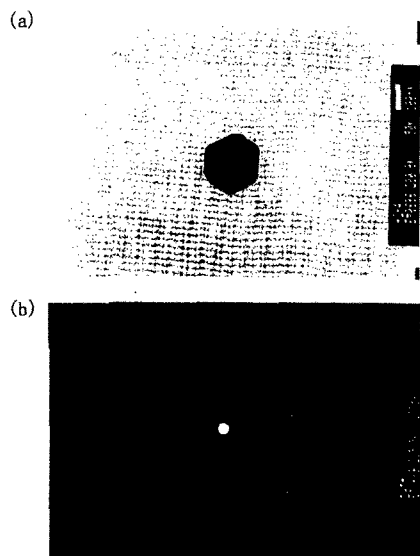


Fig. 7. TEM photograph and electron beam diffraction spot of silver particles. (a) TEM photograph, (b) electron beam diffraction spot.

mechanism proposed by Matijevic et al.<sup>16)</sup> may be more appropriate. Namely, monocrystal-like powder particles obtained in this experiment are considered to be formed by adsorption of solute molecules onto the nuclei; they grow tightly by a similar mechanism to form monocrystal-like powders without pores and voids.

### 3.3 Fine particle characteristics of the synthesized particles

Table 2 shows the specific surface area and tap density of the two types of Ag particles obtained using the BET method: (a) Ag particles containing many aggregate particles which were synthesized using the general wet chemical reduction method, and (b) Ag particles synthesized using the current nucleus growth reaction method.

As exhibited in Table 2, the Ag particles synthesized using the nucleus growth reaction method have a smaller specific surface area and higher tap density than the Ag particles synthesized using the general method which contain a large number of aggregate particles, even when taking the particle diameter obtained from the above-mentioned particle size distribution into consideration. Thus, the Ag particles synthesized using the nucleus growth reaction method can be said to be monodispersed particles.

Table 2. Densities of Ag powders  
(a) Conventional Method, (b) New Method

Sample preparation method	Average particle size ( $\mu\text{m}$ )	Specific surface area ( $\text{m}^2\text{g}^{-1}$ )	Tap density ( $\text{gcm}^{-3}$ )
(a)	3.11	2.40	0.75
(b)	0.98	1.40	2.07

## 4. Conclusions

We experimentally investigated the generation mechanism of monodispersed particles with the aim of synthesizing Ag particles which can be used for precision electrodes in laminated ceramics capacitors and dielectric resonators by means of a wet reduction method. We also compared the fine particle characteristics of Ag particles synthesized using the wet reduction method with those using the general method; we obtained the following results.

- (1) To decrease the reduction speed, an important factor in generating monodispersed particles, it is important to control three factors: synthesis temperature, concentration of aggregation-relaxing agent added, and concentration of silver nitrate solution.
- (2) Synthesis of monodispersed spherical Ag particles used as the metal powder for electrodes became possible using the nucleus growth reaction method. In addition, control of the diameter of powder particles was also possible.
- (3) TEM observation revealed that the monodispersed, spherical, synthesized Ag particles had a hexagonal form with high crystallinity; electron beam diffraction spots confirmed that they were composed of monocrystals.
- (4) The independently monodispersed, spherical synthesized Ag particles have a higher rate of dispersity and crystallinity compared to those synthesized using the general wet chemical reduction method.

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