Preparation of Micro Controlled Particles
Using Aerosol Process Technology †

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1. Introduction

The preparation of fine particles in the gas phase is now established as an important technique for producing carbon black, pigments, ceramics and magnetic materials. Especially, for the ultrafine particles with diameters less than 0.1 μm and with low sintering temperatures, this method is expected to be useful in future industrial applications. The characteristics required to fine particles are a small agglomeration number, spherical shape, narrow particle size distribution and a controlled chemical composition as well as a controlled crystal structure. The development of a process to prepare fine particles with a well defined crystal structure and chemical composition has now become an important topic.

Fine particles are generally prepared by techniques involving solid, liquid or gas phase reactions. To prepare a homogeneous material, the solid phase method requires repeated calcination and crushing procedures. This leads to problems of impurity contamination, difficulties in graining, and it also tends to give irregular, non-spherical particles. Especially when preparing fine particles of superconducting oxides, extreme care must be taken with respect to impurity contamination. It is therefore difficult at present to prepare fine superconducting particles having a crystalline phase using a sol-gel method such as the liquid phase method directly.

In most studies, the properties of fine particles prepared in the gas have been investigated experimentally as functions of the reaction temperature, flow rate and the reactive gas concentration.

But these are only preliminary studies carried out under limited conditions. Only a few studies have been reported involving the positive control of particle characteristics, such as size distribution, crystalline structure, shape etc.

In this paper we first review the preparation of fine particles by a gas phase method, i.e., the aerosol process. The characteristics and the particle generation processes are described in terms of gas-to-particle and droplet-to-particle conversion. Then methods to control the particle shape, surface state, crystal structure and size are detailed. Finally, examples of fine particles produced by controlling the preparation conditions are presented.

2. Generation of Fine Particles using Aerosol Processes

Fine particles are generated in the gas phase by various processes. Two typical processes are:

1. The bulk solid is crushed or a liquid is sprayed.
2. Molecular material collides in the gas phase and assembles into an aggregate.

Process 1 is known as the crushing and grinding process or the breaking-down process. Process 2 is the particle formation by
The condensation of vapor molecules and is called the building-up process. Particle generation processes can be classified as shown in Table 1. Among these particle generation processes, the process in which the particles dispersed in the gas phase are of sub-micrometer size is called the aerosol process and is shown in Figure 1. The main aerosol processes are the gas-to-particle conversion and droplet-to-particle conversion.

2.1 Gas-to-Particle Conversion Process

The gas-to-particle conversion process may be subdivided further into processes which depend on condensation due to physical cooling of a high temperature vapor (Physical Vapor Deposition; PVD) and processes involving chemical reaction in the gas phase (Chemical Vapor Deposition; CVD).

In most conventional preparation methods of fine particles by CVD, the chemical reaction of a gas at high temperatures is the most important concern. The main processes, classified by heat, are
I. Chemical Flame Process
II. Plasma Process
III. Laser Process
IV. Thermal Process using an Electric Furnace

The characteristics of these particle preparation processes are given in Table 2.

Table 3 summarizes the particle preparation methods reported over the last ten or so years. Many reports deal with particle preparation by plasma and thermal processes.
using an electric furnace. The type of reaction used in the experiments for particle generation varies and the reaction processes used to prepare metallic particles, for examples, are classified in Table 4.

Process A in Table 4 is a PVD process in which condensation occurs because of the physical cooling of a high temperature vapor. The Gas Evaporation Technique (GET) method is a typical example of such a process and here the particles are prepared by evaporation and condensation of metals in an inert gas under low pressure. Processes B-G show particle generation by CVD.

To initiate the gas-to-particle conversion process, the material to be condensed as fine particles is put into a super-saturated state by either chemical reaction or physical cooling. When the degree of super-saturation is high, enough particles are formed by homogeneous nucleation. As illustrated in Fig.1, spherical particles are generated when the temperature of the atmosphere is higher than the melting point of particle, while aggregated particles are generated at lower temperatures.

Particle generation by homogeneous nucleation is possible not only by PVD or CVD but by other methods as well. During particle formation the monomer generation rate, and therefore the generation rate of the super-saturation, may differ significantly from the particle generation rate. When the monomer formation rate is relatively slow, the saturation vapor pressure of condensing material is high, and the particle to be generated is liquid-like, the degree of super-saturation decreases and the evaporation of monomer from the clusters can not be neglected. In this case, the “classical droplet formation model” is valid for evaluating particle generation. On the other hand, when monomer generation is very rapid and the saturation vapor pressure of the material to be condensed is low, the degree of super-saturation becomes very high and the particle generation process can be evaluated using an aggregation model.

When the process is simplified by assuming that the chemical reaction is completed instantaneously and that the monomer generated immediately aggregates by thermal motion to form fine particles, the number concentration \( N \) and the mean diameter of the fine particles formed after \( t \) sec are given by:

\[
N = 0.1624 \alpha^{6/5} (KT)^{1/5} (Mn_t/\rho_p N_o)^{1/3} \\
d = 2.274 \alpha^{2/5} (KT/\rho_p)^{1/5} (Mn_t/\rho_p N_o)^{1/5}
\]

where \( \alpha \) is the sticking probability upon collision of two particles, \( K \) is the Boltzmann constant, \( N_o \) is Avogadro’s number, \( M \) is the molecular weight, \( \rho_p \) is the particle density, \( n \) is the initial number concentration of vapor molecules, and \( T \) is the absolute temperature. From Eq.(2), \( d \) is proportional to the 0.4 power of \( n \).

When the reaction does not finish instantaneously, various species ranging from the \( A \)-sized monomer particles a few \( \mu \)m in size may exist simultaneously. To evaluate the generation of fine particles, it is necessary to relate the kinetics of molecular order to the behavior of the fine particles to be generated.
Table 3 Preparation method of ultrafine particles using aerosol reactor

| Method | Name of method | Content of method | Produced powder and its characteristic |
|--------|----------------|-------------------|----------------------------------------|
| Combustion process | Flame reaction method | • Thermal decomposition of anhydrous chlorides in diffusion flame of a hydrogen-oxygen reactor | Metallic oxide TiO₂, Fe₂O₃, SiO₂ 10nm – 200nm |
| | | • Thermal destruction of hydrocarbons in a high-temperature of 1000°C | Carbon black ~ 30nm |
| | Electric arc method | • High voltage discharge is applied to a metal held between carbon electrodes | Oxide, carbide metal 10nm – 100nm |
| | Plasma jet flame | • Heating of material by plasma jet flame in inert gas | Fe-Co-Ni alloy |
| Plasma technology | Plasma gas phase reaction | • Vapor phase reaction between gas species in plasma jet | TiC, SiC 10nm – 150nm |
| | Hybrid plasma method | • Metal vapor-carrier gas mixture is supplied to arc jet produced by high-frequency plasma jet | Si₃N₄, β-SiC, AlN 10nm – 30nm |
| | RF(Radio Frequency) plasma evaporation method | • Two kinds of metallic vapors in a plasma flame are quenched | NbAl₁₅, Nb₂Si₅ |
| | Arc plasma sputtering method | • Atoms or molecules of high melting point materials or compound materials are supplied into gas phase | Fe, Ni, Ag, Si, SiC |
| | Nitrogen plasma method | • Particles are produced by an arc melting of metal in nitrogen gas | TiN, AlN, Si 20nm – 300nm |
| | Activated hydrogen molten metal reaction method | • Particles are generated from the melted metal by arc discharge in the atmosphere of H₂ gas | Most of metal and metallic compounds |
| Laser driven process | Laser driven gas phase reaction | • Gas species are heated by laser (CO₂) to produce gas phase reaction | TiO₂, TiN, Al₂O₃, Si₃N₄, SiC, Si 50nm |
| Thermal reactor using electric furnace | Thermal decomposition | • Metal carbonyl compounds, tetramethyl-disilane are thermally decomposed | Fe, Ni, SiC, Si |
| | Vapor phase oxidation method | • Metal chlore, metal acacalactonate, metal alkoxide vapors are oxidized to produce particles | Metal oxidate Metal carbide |
| | Hydrogen reduction method | • Vapor of metal chloride is reacted with hydrogen gas | Ni, Fe-Co ~ 25nm |
| | High-temperature reaction in NH₃ gas | • Vapor of metal chloride is reacted with NH₃ gas in the temperature of 1200 – 1400°C | WC, Mo₂C, NbC, Si₃N₄, TiN 50nm – 300nm |
| Gas evaporation technique (GET method) | Electron beam heating, laser heating, arc heating, induction heating, resistance heating | • Metals or high melting point materials are evaporated in an inert gas | Metallic refractory oxide |
Table 4 Classification of chemical reaction involving homogeneous nucleation

M, M' : Metallic elements. X, Y : Non-metallic elements or functional groups. g: Gas. s : Solid. f : Fine particles

| Reaction Type          | Equation                                                                 |
|------------------------|---------------------------------------------------------------------------|
| A : Condensation       | \( \text{M}(g) \rightarrow \text{M(s,fp)} \)                              |
| B : Decomposition      | \( \text{MX}(g) \rightarrow \text{M(s,fp)} + \text{X}(g) \)               |
| C : Partial decomposition | \( \text{MXY}(g) \rightarrow \text{MX(s,fp)} + \text{Y}(g) \)           |
| D : Oxidation          | \( \text{M}(g) + \text{X}(g) \rightarrow \text{MX(s,fp)} \)             |
| E : Reduction          | \( \text{MX}(g) + \text{Y}(g) \rightarrow \text{MY(s,fp)} + \text{X}(g) \) |
| F : Displacement       | \( \text{MX}(g) + \text{Y}(g) \rightarrow \text{MY(s,fp)} + \text{X}(g) \) |
| G : Exchange           | \( \text{MX}(g) + \text{M'Y}(g) \rightarrow \text{MY(s,fp)} + \text{M'X}(g) \) |

Example B : Thermal decomposition of metal carbonyl compounds
- C : Thermal decomposition of metal alkoxide
- D : Production of zinc oxide
- E : Reduction of metal chloride by \( \text{H}_2 \) gas
- F : Reaction of metal chloride with oxygen
- G : Reaction of metal chloride with water vapor

which is a very difficult task. Furthermore in the particle generation equipment, there are distributions in the gas flow rate, temperature, and the concentration of the reacting vapor and the particles generated tend to aggregate or deposit to the wall of the reaction vessel. Modeling the entire particle generation process becomes very complex and still remains an important problem to be investigated.

On the other hand, experiments of particle generation by CVD provide the following results:

1. The mean diameter of the primary particles is generally proportion to the 0.4 - 0.6 power of the partial pressure of the starting material.
2. The mean diameter of the primary particles is inversely proportional to the reaction temperature and independent of the residence time. On the other hand, the mean diameter of aggregated particles, i.e., secondary particles, becomes larger with an increase in the reaction temperature and the residence time.
3. The particle size distributions of many preparation methods are close to log-normal distributions and the geometric standard deviation is generally in the range of 1.4 - 1.6.

2.2 Droplet-to-Particle Conversion Process

The droplet-to-particle conversion process is a method in which droplets in the micrometer size range are first produced by physical condensation of a high temperature vapor (IV-1 of Table 1), spraying or by one of the other methods shown in Table 1. The desired fine particles are produced by reaction of the droplets with the surrounding gas, drying or by thermal decomposition. Although this droplet-to-particle conversion process is classified in most cases as a liquid process, the particle generation occurs in the gas phase and is regarded here as an aerosol process. Since the droplet-to-particle conversion process employs a solution as the starting material, the droplets generated have a homogeneous concentration and therefore the chemical composition of the fine particles is homogeneous.

The reaction time is as short as a few seconds and the fine particles are produced continuously. Therefore, this process has numerous industrial applications.

In this process, the parameters influencing the shape and the surface state of the generated particles include the thermal decomposition
temperature and rate of solvent evaporation. As shown in Fig. 1, the particles produced may be hollow, porous, dense or broken. If the particles are classified by crystal structure, there are both single crystal aggregates and multi-crystal particles. The heating rate is a very important factor controlling both the shape and the crystal structure. When the temperature is very high, rapid vaporization near the surface occurs and concentration of the solution increases rapidly to produced super-saturated state. Nuclei are generated by homogeneous nucleation and multi-crystalline particles are formed. The center of the particle remains in a liquid state, and the particle is either broken apart or made porous by the gas formed inside the particle by continued reaction. On the other hand, when the heating rate is low, multi-crystals larger in size or single crystal particles are obtained. When the temperature is higher than the melting point of the particle, highly dense spherical particle with solid centers are obtained. When the crystal growth has some direction during the cooling process, squarish or flat particles are formed.

The diameter $d_p$ of the fine particle prepared by this method is calculated from the droplet diameter $D_p$ and solution concentration $C_p$ using the following equation, and assuming that one particle (density $\rho_c$) is formed from each droplet (density $\rho_d$):

$$d_p = D_p \left( \frac{\rho_c C_p}{\rho_d} \right)^{\frac{1}{3}}$$

(3)

When the droplets have a size distribution rather than a single diameter, the distribution of the polydisperse-particles is obtained by applying this relation to each droplet size.

When the diameter of the droplet, $D_p$, or the solution concentration, $C_p$, is decreased the diameter of the fine particles is reduced. This equation is applicable only when the particle is formed at low evaporation rates and nucleus formation at the droplet surface, with subsequent growth or breakage due to evaporation does not occur.

3. Classification of the Preparation Methods of Fine-Particles by the Aerosol Process

Micro-controlled, multi-component particles with complex structure may be formed by the aerosol processes shown in Fig. 1. These may be classified into five different types shown in Figure 2:

Type I: In this gas-to-particle conversion process, multi-component gases are introduced into the reactor. By either chemical reaction or physical cooling, a super-saturated vapor (B and D) is formed. When the degree of super-saturation is sufficiently high, fine particles are generated by homogeneous nucleation. These particles grow by coagulation and condensation of both B and D to form particles of varying composition. There may be particles containing a mixture of B and D, particles containing only B, particles containing only D, B particles coated with D, D particles coated with B as well as other combinations.

Type II: Particle C is formed in a particle generation process according to a Type I gas-to-particle conversion process and is introduced into the reactor to act as a seed, onto which both monomers and clusters of B are condensed forming a coating on the initial fine particles. This process is one of the methods used to improve the surface of fine particles by CVD.

Type III: This droplet-to-particle conversion process is exemplified by the formation of particles by spray-drying and vaporization thermal decomposition. Droplets containing precursors of a two component system (C and D) are formed by some spray dispersion process such as a nebulizer, ultrasonic spray or PVD of high temperature vapor, and are introduced into a high temperature reactor. Solvent (S) in the droplet vaporizes and the precursor in each droplet are converted to form multi-component fine particles (E and F) by a reaction with the surrounding gas or by thermal decomposition reactions.

Type IV: Fine particles (C) are suspended in a spray solution and the droplets formed each contain a particle as the seed. By reactions
| Type | Initial situation of material | Process of particle generation |
|------|-------------------------------|-------------------------------|
| I    | Reactant vapor (A, A) + C, C | B(g) → B(g) → B, D → D, D |
| II   | Reactant vapor (A, A) + C    | B(g) → B(g) → C, C → C, C |
| III  | Precursor (C, D) + Solvent (S)| C, D → Vaporization of solvent + S(g) → E, F |
| IV   | Precursor (A) + Solvent (S)  | C, A → Vaporization of solvent + C, A → C, B → C, B |
| V    | Reactant vapor (A, A) + C, C | B(g) + Nucleation → E, F → E, F, B |

**Fig. 2** Particle generation processes
within the droplet, composite particles with B and particles of C coated with B are formed.

Type V: This droplet-to-particle conversion process represents a process containing elements of both the type I gas-to-particle conversion and the type III droplet-to-particle conversion processes. Droplets containing multi-component precursors (C and D) are generated and introduced into a reactor with reactant vapor A. Solvent (S) is vaporized by heating or some other method and the precursors remaining (C and D) are converted to particles (E and F) by reactions within the droplet. Vapor A is converted to B and particles are formed by homogeneous nucleation and condensed onto particles containing E and F at the same time. This gives rise to the formation of pure B and composite particles (E and F) coated with B. In some cases, solvent (S) covers the fine particle to improve the particle's surface.

4. Characteristics of Fine Particles Generated by Aerosol Process

As described above, the use of the aerosol process produces complex particles improved by the presence of a surface coating and makes it possible to produce microcontrolled particles. In some case, both monomer and particles form a deposit on the wall surface decreasing the particle generation yield, but at the same time the formation of a thin film has occurred. Table 5 shows examples of metal oxides composites produced using the aerosol process.

The aerosol process easily produces particles having the following characteristics:

- The particles contain fewer impurities thereby insuring high purity.
- Single or multi crystal may be formed and the crystallinity and crystal structure can be controlled.
- The particles may contain multiple components.
- Coating the particles with multiple layers is possible and particles with homogeneous chemical composition are also obtainable.
- The particles may be porous or dense.
- Particle size may range from small nanometer sized clusters to a few micrometers.
- Non aggregated or aggregated particles with different void percentages are obtainable.

To control the characteristics of fine particles produced by the aerosol process, the phenomena which occur in each process in Fig. 2 must be properly evaluated. These include:

- The chemical reactions in the gas phase.
- The reaction of a single particle both at the surface and in the interior.
- The generation and growth process of a single particle including nucleation,

Table 5 Examples of metal oxide composite produced using aerosol process

| Superconductive ceramic | at M=Cu, Tl, Ba, Sr, Pb, Sb, Y etc. |
|------------------------|----------------------------------|
| M₁M₂M₃M₄O₅            | Electric conductive magnet       |
| ex. Bi=Pb−Sr−Cu−O     | Electric device                  |
| Ti−Pb−Ba−Cu−O         |                                   |
| Ferroelectricity ceramic | at M=K, Zn, Nb, Fe, W, Ba, Ni |
| (M₁M₂M₃M₄)O₅          | Electric resonator               |
| ex. (SrₓCa₁₋ₓ)_₁₋ₓTi₁₋ₓY₀₃−ₓ | Optical oscillator             |
| K(T₁₀₅N₅₂₋₅)O₅        |                                   |
| Ferromagnetism ceramic | at M=Mg, Zn, Mn, Ni etc.         |
| M₁M₂Fe₃₋₅O₅           | Elements composing circuit       |
| ex. MgₓZnₓFeₓO₅        |                                   |
| Sialon ceramic         | at M=Li, Mg, Ca, Y or rare earth elements |
| Mₓ(Si, A)₁₋ₓ(O, N)₁₆  |                                   |
evaporation and condensation.

- The physical process such as aggregation involving more than one particle.
- Deposition phenomena due to diffusion and thermal migration of both the gas and fine particles.
- The heterogeneous reaction rate of gas and the transport of heat and momentum in the temperature field.

5. Experiments on Fine Particle Generation by the Aerosol Process

In particle generation using the aerosol process, there are only a few examples reported in which the particle characteristics are controlled over a wide range. Here we report typical experimental examples of the control of fine particles produced on a laboratory scale.

5.1 Preparation of Oxide Particles by Hydrolysis and Thermal Decomposition of Metal Alkoxide Vapor\(^7\) (Gas-to-Particle Conversion Process)

Processes to generate fine oxide particles by hydrolysis or thermal decomposition of alkoxide vapor of Ti, Al, and Si are frequently employed. This method is a typical example of the gas–to–particle conversion process and is explained as follows.

\[\text{Figure 3 illustrates an experimental apparatus}^3\text{ used to coat the surface of ultrafine particles of titanium dioxide (TiO}_2\text{) by alcoxy silane (AlcSi) which is an example of surface modification of fine particles shown as Type II in Fig. 2. By using nitrogen as a carrier gas, titanium tetraisopropoxide (TTIP) and a large excess of water are vaporized, mixed and introduced into a reaction furnace to prepare ultrafine amorphous particles of TiO}_2\text{. Then, propyltriethoxysilane (PrSi(OEt)}_3\text{) or tripropylmetoxysilane is introduced to coat the surface of the TiO}_2\text{ particles. Figure 4 shows a TEM picture of the TiO}_2\text{ particles obtained by this method. This figure shows that the diameter of the primary particles can be controlled in the range of 10-100 nm by the proper choice of preparation conditions. The TiO}_2\text{ fine particles obtained}\]

\[\text{Fig. 3 Experimental apparatus for reforming TiO}_2\text{ particles. (Presented by Idemitsu Kosan Corp.)}\]

\[\text{Fig. 4 TEM photographs of reformed TiO}_2\text{ particles. (Presented by Idemitsu Kosan Corp.)}\]

\[\text{Fig. 3 Experimental apparatus for reforming TiO}_2\text{ particles. (Presented by Idemitsu Kosan Corp.)}\]
by this method can be easily dispersed in organic solvents and the diameter of the dispersed particles is small enough to allow good transparency in the visible light region. The characteristics to shield W light in the region near 300 nm (UV-B) are still maintained and it is found to be useful as a transparent W shielding agent.

Figure 5 shows the apparatus used to prepare TiO\(_2\) particles by thermal decomposition of TTIP vapor with the use of seed particles shown as Type II in Fig. 2. First, N\(_2\) gas is introduced into an evaporator maintained at 40 °C to generate TTIP vapor. This is then mixed with N\(_2\) gas containing seed particles at the entrance of the reactor and sent into the furnace. This furnace is composed of 5 stages to allow independent temperature settings. Figure 6 shows the change in the number concentration of the particles at the exit of the pipe for 3 different seed particle sizes. The abscissa is the dimensionless number concentration of seed particles, N\(_s\), divided by the number concentration of the particle generated by CVD in the absence of seed particles, N\(_{so}\). The ordinate is the dimensionless value of the number concentration of particles generated, N\(_g\), divided by N\(_{go}\). This figure shows that the effect of the seed particles is small at a low number concentration of seed particles while at a higher number concentration new particles are not generated due to a restriction of nucleation by the seed particles. This means that the seed particle is coated. At the same number concentration of seed particles, the seed particle with a larger size has a larger effect. The broken line in the figure shows the results of a numerical model and coincides qualitatively with the experimental results.

5.2 Preparation of Silicon Particle by Thermal Decomposition of Silane Gas (Gas-to-Particle Conversion Process)

Figure 7 shows the apparatus used to prepare silicon particles by the thermal decomposition of silane gas (SiH\(_4\)) with the use of seed particles shown as Type II in Fig. 2. First, silicon particles are generated by the reaction of silane gas at a concentration of 1% in a reaction furnace at 900 K. These particles may have some distributions in size or may be aggregated. These particles, now acting as seeds, are mixed again with silane gas and introduced into the second reaction furnace. This reaction furnace has five stages with temperature gradients and allows for growth of the seed particle only without generating...
new particles due to thermal decomposition. The temperature distribution of the second furnace should be set by considering the reaction mechanisms involved.

**Figure 8** shows the effect of the concentration of silane gas added to the seed particles due to thermal decomposition. The measured total number concentration, $N_r$, produced in the aerosol reactor as a function of seed particle number concentration, $N_s$, for different seed particle sizes.

![Fig. 6](image)

**Fig. 6** Measured total number concentration, $N_r$, produced in the aerosol reactor as a function of seed particle number concentration, $N_s$, for different seed particle sizes.

The gas concentration is an important factor. **Figure 9** shows the change in the size distribution of silicon particles when 1% silane gas was added. The broken line shows the size distribution of the seed particles themselves and the solid line represents that of the silicon particles after growth. The particle size distribution after growth is sharper than the initial distribution.

**5.3 Preparation of Oxide Superconductor Particles by the Thermal Decomposition Reaction of Organometallic Vapor**

The CVD method is now frequently used for the preparation of thin films of oxide superconductors. But there are only a few reports on the preparation of fine particles. Using the Type I method outlined Fig. 2, the
production of fine particles of bismuth oxide superconductor system has been attempted by using \( \beta \)-diketonate complexes of Ca, Cu and Sr and organometallic compound of Bi as the starting materials.

**Figure 10** shows the experimental system. The horizontal five stage furnace consists of a vaporization stage followed by a reaction chamber. Powders of the starting materials, Bi(Ph)\(_3\), Cu(DPM)\(_3\), Ca(DPM)\(_3\), Sr(DPM)\(_2\), were put into evaporating dishes and heated in the vaporization section. The vaporization temperatures were adjusted so that the ratio of Bi:Ca:Sr:Cu was 2:1:2:2. These temperatures were 150 - 200 °C for Cu(DPM)\(_3\), and Bi(Ph)\(_3\), and 200 - 250 °C for Ca(DPM)\(_3\), and Sr(DPM)\(_2\), and all temperatures were controlled independently. The vaporized starting materials were introduced into the reaction chamber by using Ar as a carrier gas. \( \text{O}_2 \) acted as an oxidizing agent and was introduced to the reaction chamber at the same time through a different path. Fine particles were prepared with carrier gas flow rates in the range of 300 - 900 ml/min keeping an Ar and \( \text{O}_2 \) gas ratio of 2:1, and with the temperature in the reaction chamber in the range of 750 - 900 °C.

**Figure 11** shows X-ray diffraction pattern of the particles obtained at various reaction temperatures with a carrier gas flow of 750 ml/min and with a residence time in the reaction furnace of 14 sec. This figure shows that at a reaction temperature of 820 °C a peak of for the 10 K superconducting phase, indicated by an x appears. When the reaction temperature is raised to 825 - 850 °C, peaks for both the 10 K and the 80 K(o) phases appear. In other words, the fine particles formed in this range of reaction temperature have a mixed phase of 10 K and 80 K. When the reaction temperature is raised further to 860 °C, only the 10 K phase is present. These results indicate that the reaction temperature appropriate for the growth of the 80 K phase is located near 825 °C, but that the particles are formed without a sufficient growth of 80 K phase due to a rapid flow rate and a short residence time.

The particle size distributions were measured at flow rates of the carrier gas of 300 and 600 ml/min. Ultrafine particles having a
Fig. 11 X-ray diffraction patterns of Bi$_2$Ca$_x$Sr$_2$Cu$_2$O$_x$ particles at different temperatures.

relatively uniform size of about 60 nm at 300 ml/min and about 50 nm at 600 ml/min were obtained. At higher flow rates the particles are smaller. The shape of the particles was close to spherical.

One problem in the preparation of fine particles by this CVD method occurs when the reactor wall at the exit is cooled generating a temperature gradient and particles deposit by thermal migration. To prevent this depositional loss is necessary to keep the reactor wall hot.

5.4 Preparation of Fine Particles of Oxide Superconductor by Spray Pyrolysis Method (Droplet-to-Particle Conversion Process)

As an example of the preparation of fine particles by spray pyrolysis fine particles of the superconducting oxide with the composition Bi$_2$Ca$_x$Sr$_2$Cu$_2$O$_x$ were generated using a five stage furnace and the effect of the temperature gradient of the furnace and the flow rate of the carrier gas on the crystalline phase and shape was examined.

Figure 12 shows a schematic of the experimental apparatus used for the preparation of the fine particles. The spray solution containing dissolved metal nitrates at the desired compositions was sprayed using an ultrasonic nebulizer and introduced into the reaction furnace with a carrier gas. Fine particles were generated in the reaction furnace and are collected by an electrostatic precipitator with a diffusion charger.

Fig. 12 Apparatus for generating superconductive metal oxide particles.

The reaction furnace has five stages capable of independent temperature control. The SEM picture of the fine particles obtained at a carrier gas flow rate of 2 l/min and with $T_1 - T_2 = 800$ °C is shown in Fig. 13. The temperature rises rapidly at the entrance of the
reaction furnace. The flow rate of the carrier gas was so rapid that nucleation occurred easily in the particle generation process and particles lacking a part of the core were observed.

Figure 14 shows a SEM picture of the particle obtained at $T_1 = 950^\circ C$, $T_2 = T_3 = T_4 = 800^\circ C$ with a carrier gas flow rate of 0.2 l/min. At $T_1 = 950^\circ C$, the particles are in a melted state and reactions take place in a liquid phase. Then, at $T_2 = T_3 = 800^\circ C$, the particles become squarish and dense probably because the carrier gas flow rate was low and the temperature of $800^\circ C$ was appropriate for the growth of crystals.

5.5 Preparation of Oxide Particle by Vaporization and Condensation of Metal Alkoxide Vapor

Figure 15 shows an outline of the apparatus. This is an example of particle preparation by the method labelled Type V in Fig. 2. First, silver chloride is heated at 645°C and cooled to generate ultrafine particles on the order of nanometers. To this, metal alkoxide vapor (vaporization temperature of 96.5 °C) is mixed and cooled to generate a super-saturated atmosphere and to condense the vapor into droplets with a silver oxide particle as a nucleus (seed particle). When this is heated again and cooled, alkoxide droplets having uniform particle size are generated. When water vapor added, titanium oxide particles are generated by the reaction between the water and the alkoxide.

Figure 16 shows the size distribution of alkoxide droplets generated by the evaporation-condensation method and of the titanium oxide particles formed after mixing with water vapor. Although not completely
homogeneous, particles of relatively similar size are obtained. By using this technique, the preparation of $\text{Al}_2\text{O}_3$, two component particles of $\text{TiO}_2$ and $\text{Al}_2\text{O}_3$, and $\text{TiO}_2$ particles with a polymer coating are reported. This technique allows us to prepare particles with mean particle diameters of about $0.06 - 1\mu$m. Possibilities may include combination of droplet-to-particle conversion and seed-particle methods. In order to evaluate and improve the particle preparation processes demonstrated empirically, an improved approach based on aerosol science and technology is inevitable.

6. Concluding Remarks

The preparation of finely controlled particles by aerosol processes are becoming more important. Polydisperse particles having geometrical standard deviations in the range of 1.4 to 1.6 can be prepared easily by gas-to-particle as well as droplet-to-particle conversion processes. Finer control may be possible by changing the concentration of the reaction gas, the reaction temperature and other conditions. To obtain particles with narrower size distributions, further elaborations on the technique are required.

Fig. 16 Size distribution of alkoxide droplets and $\text{TiO}_2$ particles.

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