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Synthesis of Superconducting Oxide by Mist Pyrolysis Method

Masanobu AWANO,* Hiroyoshi TAKAGI, Yasuyoshi TORII,
Norimitsu MURAYAMA, and Eiichi SUDO+
Government Industrial Research Institute,Nagoya, Hirate-cho,
Kita-ku, Nagoya 462
+Tokyo Kokyu Rozai Co.Ltd., Asamuta, Ohmuta, Fukuoka 836

The powder of oxide superconductor was synthesized by the mist pyrolysis method. $Ba_2YCu_3O_{7-y}$ single phase particles were produced at reaction temperature of about 950 °C. The particle size changed with the concentration of starting solution and was about 0.1 μm diameter at the concentration of 0.00125 mol/l. They had homogeneity as the result of pyrolysis of droplets, including stoichiometric components.

Improvement of the critical current density (Jc) of the oxide superconductor is required for utilization of this material to wire, coil and so on. For such purpose, to synthesize the fine particles with a certain chemical composition as the raw material of superconductor is very important. Because the use of such particles brings a densified uniform polycrystalline texture in a sintered body, the superconductive properties such as Jc depend on the structural features such as density, grain size, pore-size and -distribution, compositional uniformity and purity.

This paper deals with the preparation of fine $Ba_2YCu_3O_{7-y}$ particles by the mist pyrolysis method.[1)] The concentration change of the solution and reacting temperature caused the changes of the size and cristalline phase of particles. The minimum average particle size was approximately 0.1 μm. The chemical composition of particles investigated by the analytical electron microscope(AEM) was coincident with that of droplets. The orthorhombicity of the particles which has influence on critical temperature was discussed concerning with the synthesized condition.

The schematic diagram of the mist pyrolysis method is shown in Fig.1. Atomizing solution was prepared by dissolving Y- and Cu- oxides and Ba- carbonate into nitric acid. An ultrasonic vibrator was used to atomize the solution. Atomized mists were carried to the reacting zone by the oxygen flow (the flow rate was approximately 1000 ml/min). They were dried, pyrolyzed and crystallized in a few seconds. Subsequentry, pyrolyzed particles were collected by filtration on the Teflon filter. The crystallinity of these particles was examined by the Powder X-Ray Diffraction method. Their particle size was measured by SEM and TEM observation. The uniformity of chemical composition in these particles was checked by the Analytical Electron Microscope (AEM).

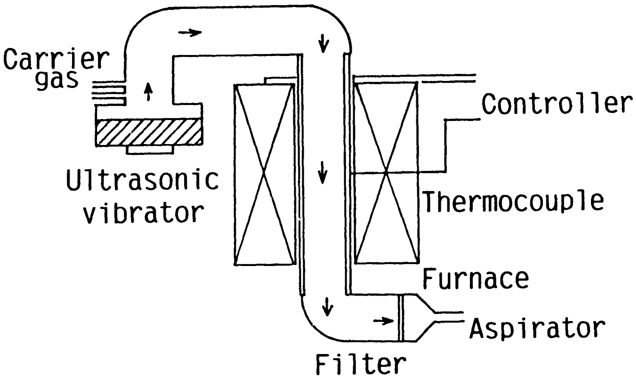

Fig.1. Schematic diagram of the mist pyrolysis method.

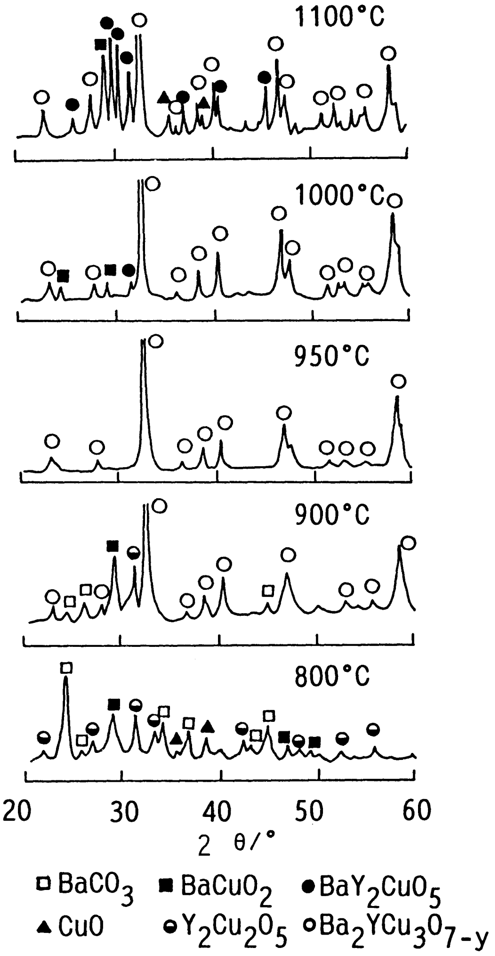

Fig.2. X-Ray diffraction patterns of powders obtained at various reaction temperatures.

Figure 2 shows the X-Ray diffraction patterns of the powders obtained by pyrolyzing at various temperatures. At 800 °C, the constituent phases were $BaCO_3$, CuO, $Y_2Cu_2O_5$, and $BaCuO_2$ and they indicated the intermediate states of pyrolyzing. $Ba_2YCu_3O_{7-y}$ phase were found in the particles pyrolyzed at nearly 900 °C. At 950 °C - 980 °C the patterns showed the single phase of $Ba_2YCu_3O_{7-y}$ whose crystallinity was an orthorhombic phase.[2)] The result is consistent with the result of TEM observation of particles which shows the twin lamellar structure, suggesting the occurrence of tetragonal-orthorhombic phase transition in the cooling stage of particles. This orthorhombic phase of these particles was different from that of another fine particles obtained by the coprecipitation[3)] or the alkoxide method.[4)] It is said that the orthorhombicity of $Ba_2YCu_3O_{7-y}$ closely related to the transition temperature of superconducter (Tc).[5)] The orthorhombicity of these particles were not sufficient to have superconducting property at 90 K (according to the magnetization measurement of powders, they showed Tc end below 80 K). Exceeding of the pyrolyzing temperature above 1000 ℃ caused partial melting of powders that was indicated by the appearance of BaY_2CuO_5 peaks. Such powders formed above 1000 °C showed spherical figure by melting, and above 1200 °C they deposited as the solidified film. The intensity of BaY_2CuO_5 peak increased remarkably with temperature increase.

Figures 3 and 4 show the particle size change in relation to liquid concentration. The pyrolyzing temperature was 950 °C and the liquid concentrations were varied as follows; 0.01 mol/l, 0.005 mol/l, 0.0025 mol/l and 0.00125 mol/l. The particle size decreased with decreasing liquid concentration. The degree of dispersion of the powder was superior to that of coprecipitation and alkoxide methods. This result shows that in the mist pyrolysis method the particle size is not so affected by the thermal decomposition condition as the decomposition of the oxalates. If the droplets generated by ultrasonic vibration don't collide each other, the particle size will be dependent on the size of each droplet and liquid concentration. So in this method, particles with under 0.1 μm will be obtained by control of liquid concentration and ultrsonic vibration.[6)]

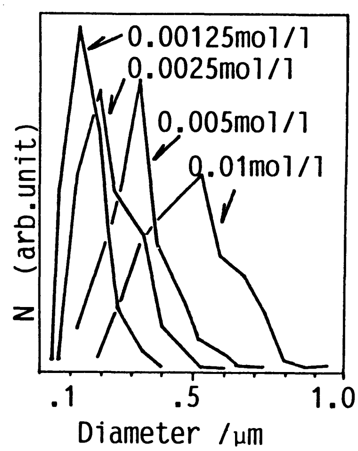

Fig.3. Distribution of particle size obtained from various liquid concentrations.

The result of AEM analysis about the particles obtained from the solution of 0.005 mol/l is shown in Fig.5. The homogeneous distribution of each element was confirmed in this figure. The chemical composition of particles estimated by the EDS analysis showed approximately stoichiometry, i.e., Ba:Y:Cu=2:1:3.

In conclusion, homogeneous particles which have the diameter of about

0.1 μm were obtained by the mist pyrolysis method under the control of the liquid concentration of atomizing. It can be expected that the application of these fine, homogeneous particles and the subsequent highly controlled sintering process contribute to get a dense, uniformly sintered body of superconductor which will have a high Jc value.

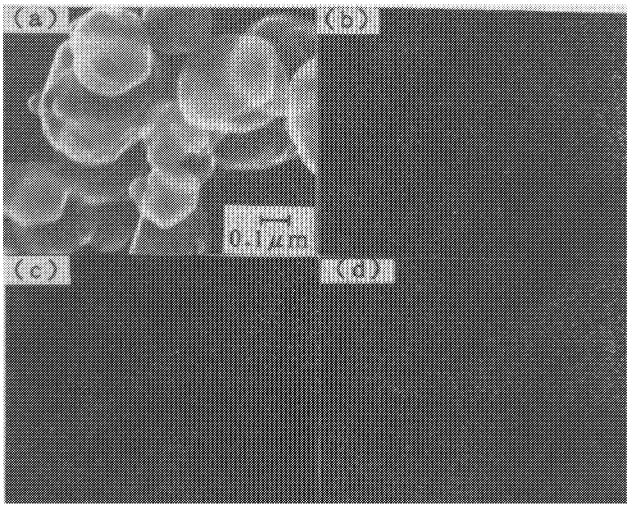

Fig.5. SEM photograph(a) and X-ray images of Y(b),Ba(c), and Cu(d).

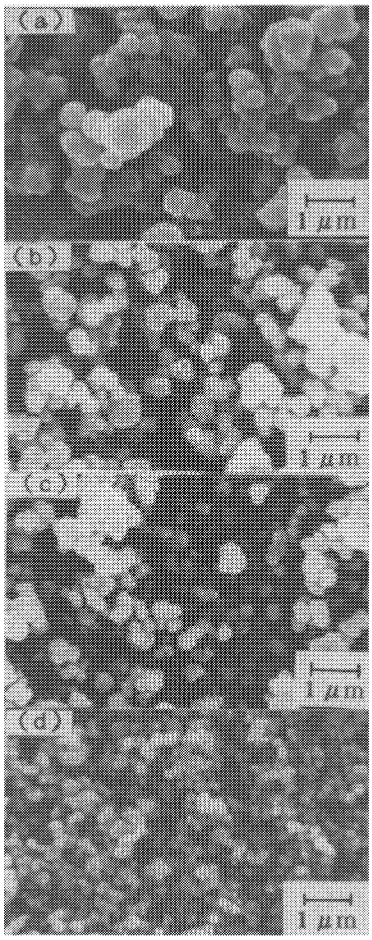

Fig.4. SEM photographs of powders from various liquid concentrations: (a)0.01 mol/l,(b)0.005 mol/l (c)0.0025 mol/l,(d)0.00125 mol/l.

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