Preparation of Superconductive Films by Fume Pyrolysis

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Superconductive films composed of $Ba_2YCu_3O_{7-\delta}$ were prepared by fume pyrolysis with a temperature programmed electric furnace. Fumes generated from an aqueous solution of Ba, Y, and Cu nitrates with an aid of supersonicant were introduced into the furnace with flowing O_2. Fine particles consisting of Ba, Y, and Cu ions were formed in the furnace and deposited on the surface of a YSZ substrate placed at the top of the furnace. Films thus prepared and annealed at 1273 K showed superconductive properties below 90 K and zero resistivity was observed at 80 K with 100 μA of the current.

Since the announcements of possible high-T_c superconductive oxides[1] and subsequent studies on relating systems,[2-5] numerous works on the structures and the electronic properties of these compounds have been reported.[6-8] Several problems for practical use have been pointed out and among them the developments of the techniques to prepare materials with high-J_c have been strongly desired to be achieved promptly. Since the J_c values have been suggested to depend on the size of powder particles, evenly sized fine particles are prefered to be employed as starting materials. One of the useful methods to produce fine oxide particles is fume pyrolysis with a supersonic nebulizer,[9] and Tohge et al.[10] have adopted this method for the preparation of superconductive bulk materials. The improvement in J_c values was not mentioned in the paper. Studies on the development of superconductive thin films have been of current interest, since high-J_c materials have been expected to be readily achieved with thin films. Films prepared by an epitaxial growth of $Ba_2YCu_3O_{7-\delta}$ on a $SrTiO_3$ substrate or those produced by an ion cluster beame (ICB) method using a MgO substrate have been reported to exhibit a J_c value of higher than 10^6 A cm^{-2} at 77 K.[11] Spray pyrolysis is also a useful method for superconductive films,[12] though sufficiently high-J_c values have not yet been reported.

In the present work, superconductive films were prepared by fume pyrolysis techniques aided by supersonicant with an aqueous solution of Ba, Y, and Cu nitrates. Fumes generated were brought into an electric furnace with flowing oxygen and turned out to be fine oxide or nitrate particles, which accumulated on the surface of a ceramic substrate (Yttrium Stabilized Zirconia, YSZ), placed at the top of furnace. The direct deposition of fine particles on the substrate is a feature of this work and is quite different from the spray pyrolysis, where fumy droplets are spreaded over a hot substrate and, subsequently, small particles are generated. Films mainly composed of a superconductive phase, $Ba_2YCu_3O_{7-\delta}$, were prepared with annealing the accumulated particles at 1273 K in oxygen atmosphere. The superconductive properties of films were discussed with the surface morphorogies of films observed by a scanning electron microscope (SEM).

Experimental

Apparatus. In Fig. 1 is shown the apparatus employed for fume pyrolysis. The apparatus mainly consists of two parts; in part A fumes are generated by a supersonicant mounted at the bottom of a vessel, including an aqueous solution of Y, Ba, and Cu nitrates with a molar ratio of 1 : 2 : 3; the concentration of metal ions was 0.02 mol L^{-1}. The frequency of the supersonicant employed was always 1.5 MHz. The part B is an electric furnace, equipped with 3 heaters located at the top, middle, and bottom of the furnace, respectively. These 3 heaters are independently controlled to give an appropriate temperature distribution in the furnace. At the radial center of the furnace is placed a reaction tube, made of quartz, directly connected with the part A. The fumes generated were introduced into the tube with flowing O_2, the flow rate being 3 L min^{-1}. A YSZ plate (2×7×0.3 mm) was placed at the top of the tube and fine oxide and/or nitrate particles formed in the furnace deposited on the surface of YSZ to be a thin film. In this experiment the temperature was controlled to be 1073 K at any parts of the tube during fume pyrolysis for 2 h. The films thus produced were annealed at 1273 K for 5, 10, 15, and 30 min, respectively, in flowing oxygen and then cooled to 673 K with the rate of 150 K h^{-1} and then to 473 K with the rate of 120 K h^{-1}, still in O_2 atmosphere.

Resistivity Measurements. The electrical resistivity of films was measured by a four-probe DC method with the current of 100 μA in the temperature range of 300—50 K. The resistivity was calculated by measuring the voltage generated between the middle 2 points on the sample film. The film thickness was estimated to be 5 μm in average by an electron probe microanalyzer (EPMA, JEOL Superprobe 733). The sample film was attached on a holder made of metallic copper and was placed in a cryostat available at liquid He temperature. The film temperatures were monitored by an Au(Fe)-Ag thermocouple.

Magnetization Measurements. Magnetization of the sample film was measured by SQUID equipment (Susceptometer 900, SHE Co.,) with an external magnetic field of 100 Öe; the sample films are placed in parallel with the magnetic field. During the measurement the sample film was vibrated with a frequency rate of 500 mm min^{-1}.

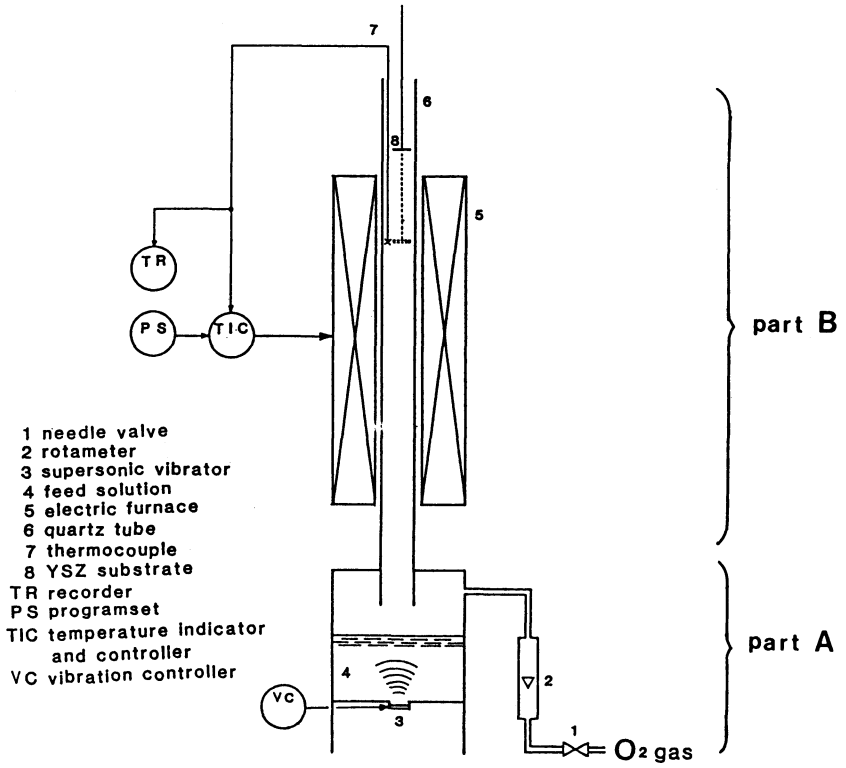

Fig. 1. Apparatus for fume pyrolysis.

Temperature dependencies of magnetization for the films, treated at 1273 K for 5, 10, 15, and 30 min in flowing O_2, respectively, were measured and the volume fractions of superconductive phases in the films were estimated.

X-Ray Diffraction Measurements. The sample film was subjected to X-ray diffraction (XRD) analysis. Since the conventional diffractometer showed peaks due to YSZ substrate as well as those due to $Ba_2YCu_3O_{7-\delta}$, a reflection X-ray diffractometer (Rigaku Denki Co., Rotaflex) was used at 50 kV with a filament current of 40 mA and carbon filter for Cu $K\alpha$ radiation. An incident X-ray angle to the sample film was settled at 0.5 degree from the horizontal plane.

SEM and EPMA Measurements. The surface structures and metal ions distributions on the sample films were observed by EPMA, operated at an accelerating voltage of 15 kV with an energy dispersive detector. The depth profiles of metal ions were also monitored by EPMA with samples mounted in polyethylene supports. All the samples submitted to EPMA measurements were covered with carbon films to prevent the charge-up phenomenon.

TEM Measurements. Particles accumulated on YSZ substrate during fume pyrolysis were removed and suspended in ethanol with the aid of a supersonicant to be submitted to a transmission electron microscope (TEM, Hitachi H-800), operated at an accelerating voltage of 200 kV with a magnification of 10^5. Thus, the size and shape of the fine particles were observed and the compositions of particles were also analyzed by an element analyzer (EMAX, Horiba Co.), equipped with an energy dispersive detector.

Results

Resistivity Measurements. In Fig. 2 are shown the changes in the resistivity of the superconductive films,

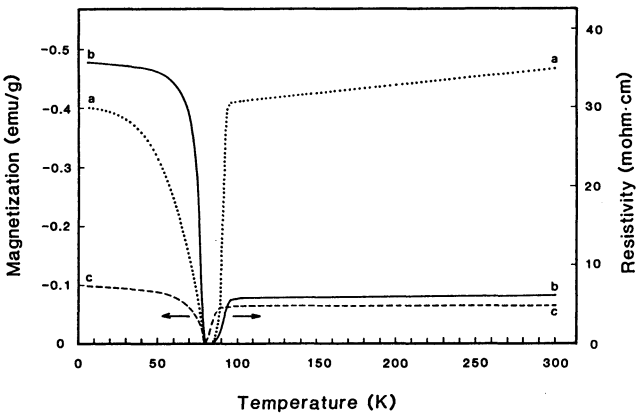

Fig. 2. Temperature dependences of resistivity and magnetization of $Ba_2YCu_3O_{7-\delta}$ films annealed at 1273 K for 5 (a), 10 (b) and 30 min (c).

treated at 1273 K for 5, 10, and 30 min in O_2 atmosphere, with temperatures varied from 50 to 300 K. The film employed was 5 μm in thickness in average. Resistivities with 100 μA of the current were almost constant (3 mohm cm) at temperatures higher than 90 K and decreased to zero at 80 K. The resistivity curves were well-reproducible for samples formed under the similar conditions; T_c=90 K, $T_{c(zero)}$=80 K, ΔT=10 K.

Magnetization Measurements. In Fig. 2 are also shown the temperature dependencies of magnetization for the films treated at 1273 K for 5, 10, and 30 min, respectively. From the saturation magnetizations

thus obtained, the volume fractions of superconducting phases formed in the films were estimated (see Fig. 3).

XRD Measurements. The reflection XRD patterns of the films annealed at 1273 K for 10 and 30 min are given in Figs. 4c and d, indicating the significant crystal growth along with c-axis of $Ba_2YCu_3O_{7-\delta}$ during the oxygen treatment at 1273 K. On the otherhand, the diffraction patterns due to $Ba(NO_3)_2$ were observed for the unannealed film (see Fig. 4a), though the decomposition temperature of $Ba(NO_3)_2$ is described at 871 K.[13] For comparison, X-ray diffraction patterns of the films annealed at 1223 K for 2 h are shown in Fig. 4b. From the slight changes in the diffraction angles of superconductive phases, changes in the lattice constants with annealing time were calculated and listed in Table 1. Oxygen contents in the superconductive unit cell were estimated from the difference between a and b-axial lengths, according to the previous paper[14] and are also given in Table 1.

SEM and EPMA Measurements. Typical SEM photographs showing the changes in surface morphorogies of the films are given in Figs. 5a to 5e with magnification of ×1600, where 5a represents the surface of the unannealed film and 5b to 5e show the surfaces of films annealed at 1273 K for 5, 10, 15, and 30 min, respectively. A SEM photograph of the films annealed at 1223 K for 2 h is shown in Fig. 5f to be compared with those of the films annealed at 1273 K. The depth profiles of Y, Ba, and Cu ions in the film annealed at 1273 K for 10 min are demonstrated in Fig. 6 and X-ray images of Y, Ba, and Cu ions on the films annealed at 1273 K for 30 min are given in Fig. 7.

TEM Photograph. In Fig. 8 are shown the TEM photographs of fine particles deposited on the substrate, particles unannealed. Particles deposited on

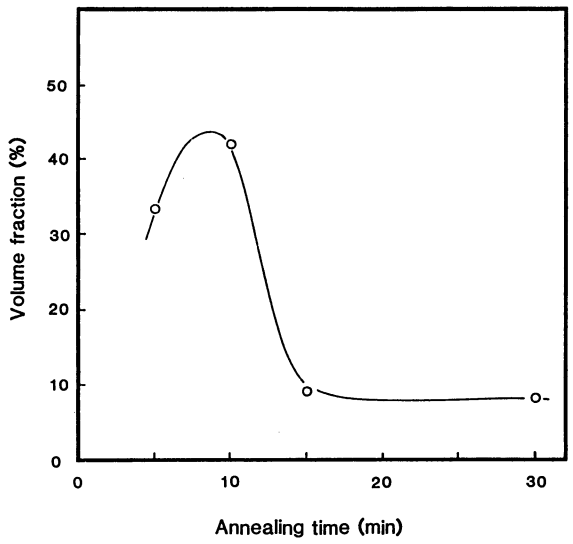

Fig. 3. Change in the volume fraction of superconductive phases in films treated at 1273 K with the annealing time.

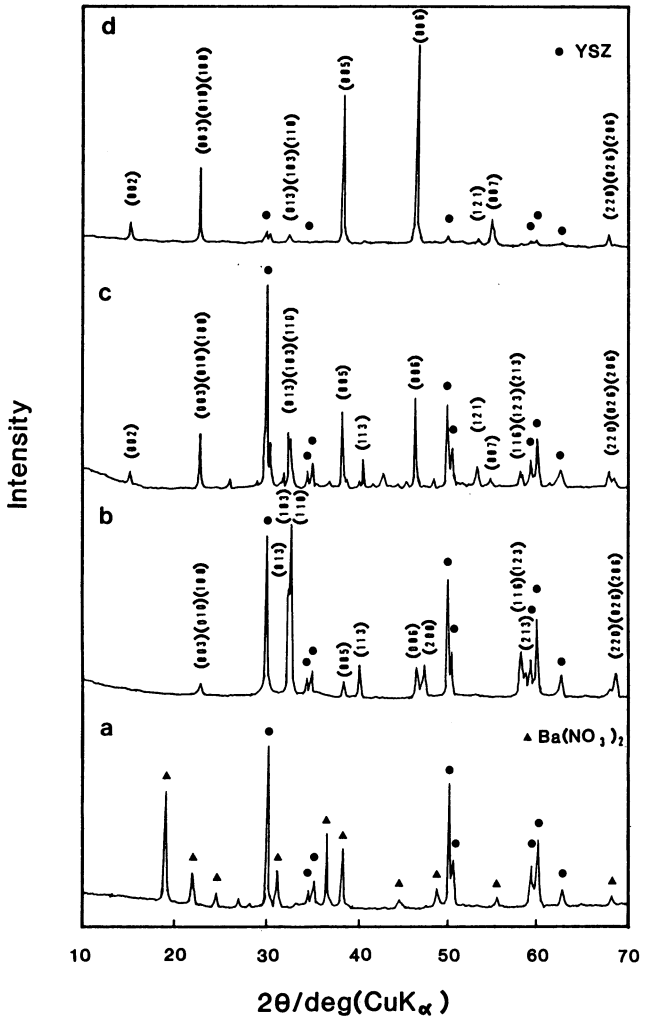

Fig. 4. XRD patterns of the films annealed at 1273 K for 10 (c) and 30 min (d), annealed at 1223 K for 2 h (b) and the unannealed films (a).

Table 1. Characterazation of Films Annealed at 1273 K for Various Times

annealed time	T_c(zero)	Volume fraction	Lattice constant (Å)			Oxygen content
min	K	%	c-axis	a-axis	b-axis	
5	84	33	11.68	3.82	3.88	6.74
10	85	42	11.67	3.81	3.87	6.65
15	—	9	11.68	3.81	3.88	6.83
30	78	8	11.66	3.82	3.84	6.29

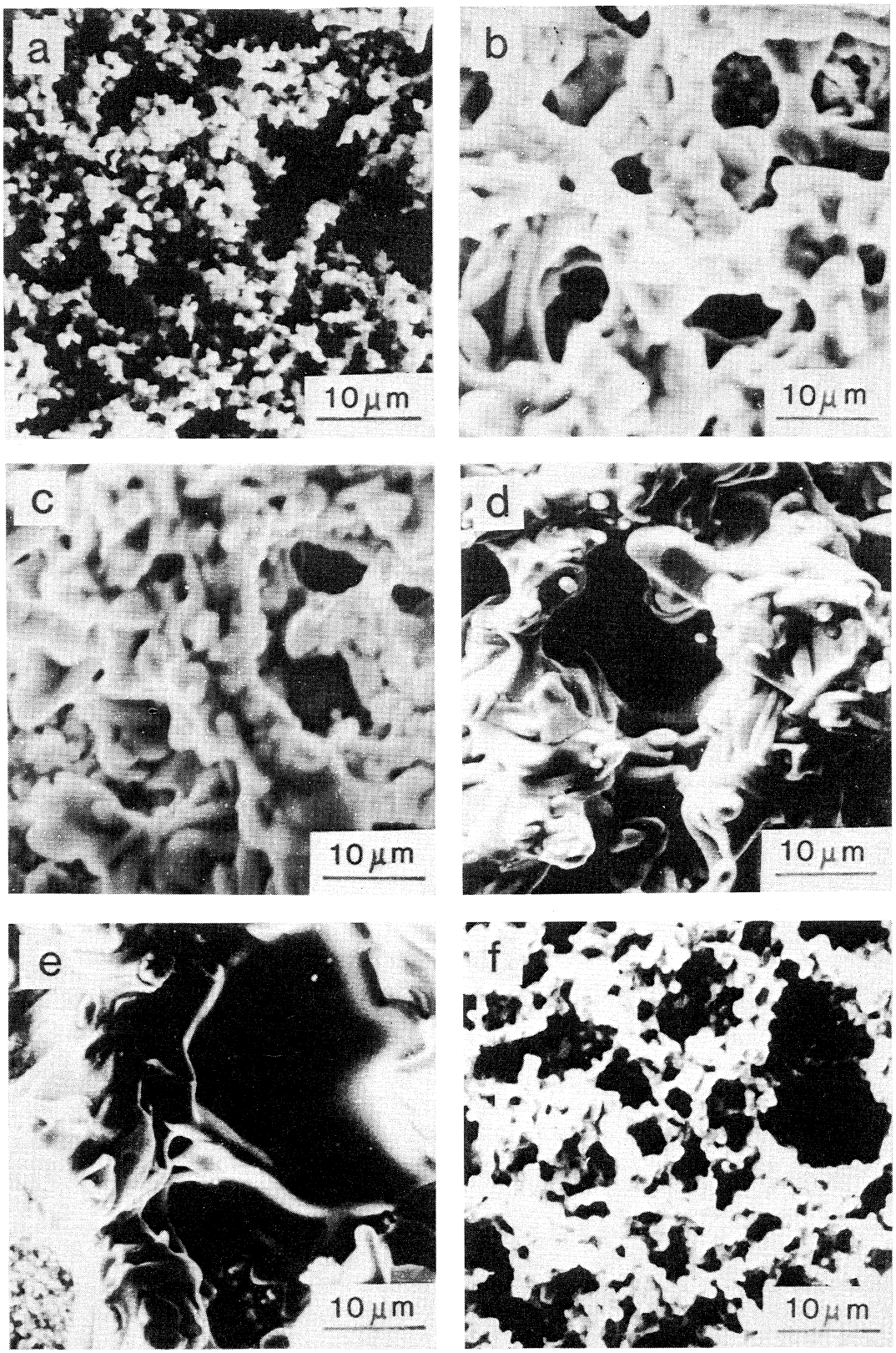

Fig. 5. SEM photographs with the magnification of ×1600; the unannealed films (a), and the films annealed at 1273 K for 5 min (b), 10 min (c), 15 min (d), and 30 min (e) and the films annealed at 1223 K for 2 h (f).

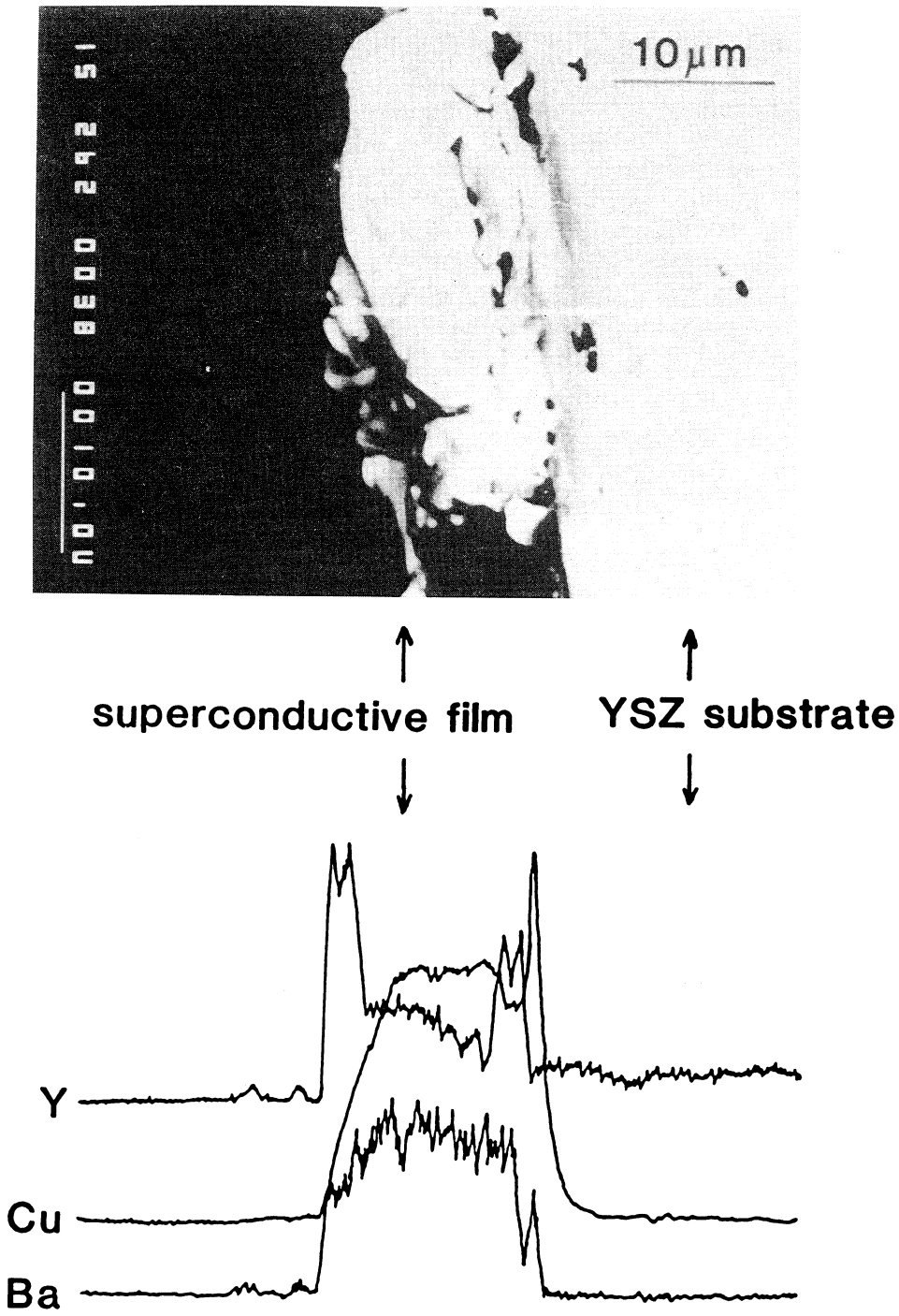

Fig. 6. Depth profilms of Y, Ba and Cu in the films annealed at 1273 K for 15 min, measured by EPMA.

the substrate seem to be spheres with the diameter of 0.5 μm, almost evenly. The composition analysis of particles is also depicted in Fig. 8, suggesting the particle consists of Y, Ba, and Cu ions though Cu ions were rather enriched in the particle than were expected to be 1/2/3 for Y/Ba/Cu.

Discussion

Particles Depositing on YSZ. Fume pyrolysis techniques with an aid of supersonication[15] have been used for the preparation of oxide particles and the particle size will be controlled by the size of droplets in fumes. A droplet size can be estimated by the following equation;[16]

$$d=0.34\left(\frac{8\pi\gamma}{\rho f^2}\right)^{1/3} \quad (1)$$

where d is the average size of droplets, f means the

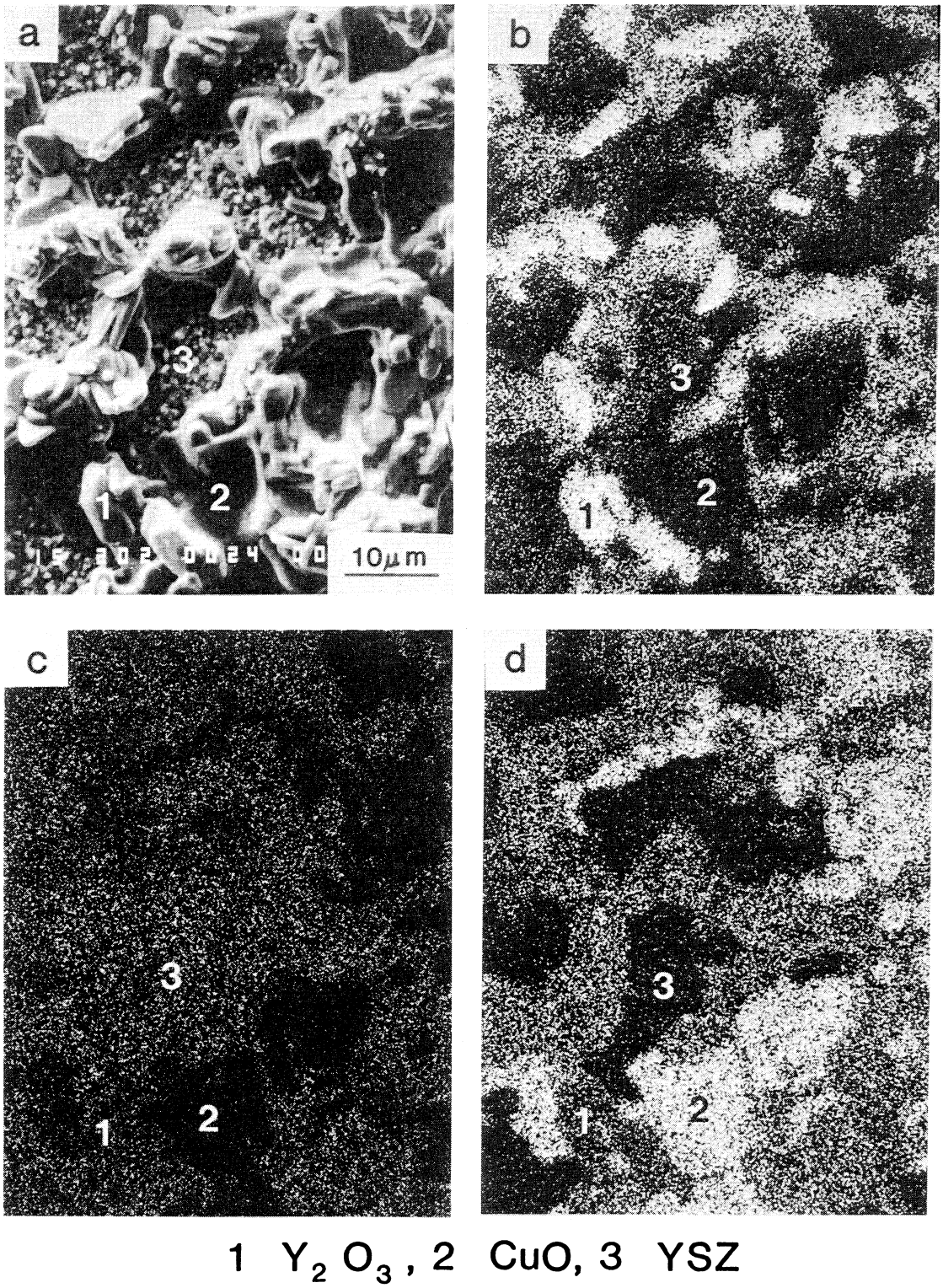

Fig. 7. SEM photograph (a) and X-ray image of Y (b), Ba (c), and Cu (d) in the films annealed at 1273 K for 30 min, measured by EPMA with a magnification of ×1600.

frequency of supersonication (1.5 MHz) and γ and ρ are the surface tension and density of droplets, respectively. In this work, metal nitrates employed are so diluted with water that the surface tension and density of droplets might be approximately the same as those of water. Thus, the average size of droplets in fumes was calculated ca. 3.2 μm and the size of particles formed during pyrolysis was estimated to be ca. 0.41 μm, since the concentration of metal ions in a droplet is 0.02 mol L^{-1}; more than 99 wt% of a droplet is water, volatilized during pyrolysis. As can be seen in Fig. 8 the size of particles depositing on the substrate is ca.

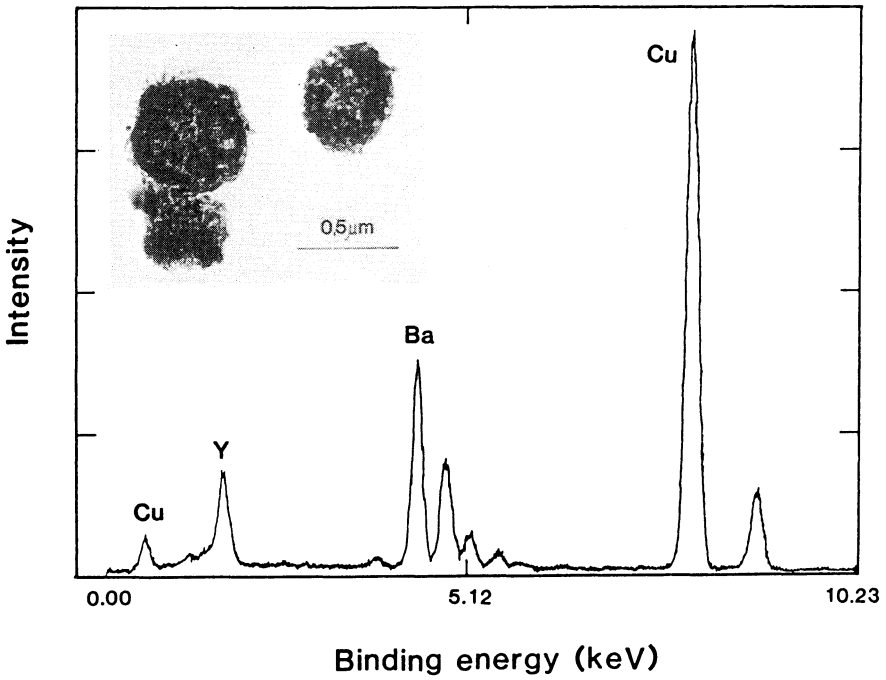

Fig. 8. TEM photograph and composition analysis of the particles depositing on the substrate during fume pyrolysis.

0.5 μm, in good accordance with the estimated size of 0.41 μm, suggesting that a droplet in fumes turned out a particle during pyrolysis. A particle, hence a droplet, was proved to be composed of Y, Ba, and Cu ions although an excess amount of Cu ions was observed (see Fig. 8). In Fig. 4a is shown an XRD spectrum of the particles depositing on the substrate and almost all of the peaks are assigned to $Ba(NO_3)_2$. By annealing the particles at 1223 K for 2 h, the peaks attributed to $Ba(NO_3)_2$ disappeared and those due to $Ba_2YCu_3O_{7-\delta}$ were observed (see Fig. 4b).

SEM Observation and Superconductivity of the Annealed Films. SEM observations of the unannealed films are given in Fig. 5a, where the films are proved to consist of spherical particles sized ca. 0.5 μm. Sintering of the particles are demonstrated in Figs. 5b to 5e, when the films were annealed at 1273 K for 5, 10, 15, and 30 min in flowing O_2. From Figs. 5d and 5e, it will be found that $Ba_2YCu_3O_{7-\delta}$ seems to be sintered by a prolonged annealing at 1273 K. The XRD spectrum of the sintered films is given in Fig. 4d, suggesting the crystalline growth of $Ba_2YCu_3O_{7-\delta}$ with the heat treatments in O_2 atmosphere at 1273 K. Although the photographs given in Figs. 5a to 5e emphasize uneven structures of the films, zero resistivities and Meissner effects were clearly confirmed at 80 K for the annealed films (see Fig. 2). A SEM photograph of the films annealed at 1223 K for 2 h showed unsintered particles mainly composed of $Ba_2YCu_3O_{7-\delta}$ (see Figs. 4b and 5f). The resistivities of this film were proved to decrease gradually below 90 K but did not reach zero even at 50 K with a small current of 10 μA.

Volume Fractions of Superconductive Phases. The saturation magnetiaztions and, consequently, the volume fractions of the superconductive phases in the annealed films strongly depend upon, the annealing time at 1273 K, as shown in Figs. 2 and 3. Thus, the volume fraction as high as 45% was achieved for the films annealed at 1273 K for 10 min but with a prolonged annealing the superconductive phases seem to decompose. In Fig. 7 are shown the X-ray images of Y, Ba, and Cu ions on the films treated at 1273 K for 15 min in O_2 atmosphere, indicating the deposition of copper oxides by the decomposition of superconductive phases. Copper oxides thus yielded were spreaded and covered over YSZ substrate, evidenced by disappearance of diffraction peaks due to YSZ of the films treated at 1273 K for 30 min (see Fig. 4d). As can be seen in Table 1, nevertheless the prolonged annealing the axial lengths of unit cell did not change so much. The difference between a and b-axial length became so small, however, when films were annealed at 1273 K for 30 min, resulting in the decrease of oxygen content in a superconducive unit cell (see Table 1).

The current used in the resistivity measurements was 100 μA and the average thickness of films annealed at 1273 K for 10 min was ca. 5 μm, as is shown in Fig. 6. Accordingly, the J_c value was estimated to be in the order of 10^2 A cm^{-2}. Unfortunately, high-J_c values in the order of 10^6 A cm^{-2} could not be achieved with the present films, probably because of uneven structures of films. Thus, one of the most important

factors to improve J_c value must lie in the homogeneous structures of films. The films with homogeneous structures will depend on the size of particles depositing on the substrate during pyrolysis. To prepare smaller particles, supersonicant with a high frequency should be used, as suggested by the Eq. 1.

Conclusion

1) A feature of fume pyrolysis is a direct accumulation of fine particles over substrate surface and was first applied here to the preparation of superconductive films.

2) With annealing the films at 1273 K, they exhibited superconductive properties below 90 K, but with a prolonged annealing the superconductive phases decomposed, probably, to the respective oxides. Thus, the relationship between annealing time at 1273 K and the volume fraction of superconductive phases in films were revealed.

3) Because of uneven structure of the films, high-J_c could not be achieved in this work. However, it was suggested that films with a homogeneous structure might be posible when fine sized droplets are employed for a fume pyrolysis. Such droplets can be generated by a supersonicant with higher frequency.

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