SYNTHESIS AND PROPERTIES OF POWDERED OXIDE SUPERCONDUCTOR BY THE MIST PYROLYSIS METHOD

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Y–Ba–Cu–O and Bi–Pb–Sr–Ca–Cu–O superconductor powders were synthesized by the mist pyrolysis method. The crystalline phase and morphology of mist-pyrolyzed powders depended on the heating temperature, heating time, and concentration of starting solutions. Superconducting phase of Y–Ba–Cu–O and Bi–Pb–Sr–Ca–Cu–O superconductor (low-T phase) were obtained directly by this method. Sintered body of Y–Ba–Cu–O superconductor obtained by using mist-pyrolyzed powder had a density of above 95% of the theoretical density. The critical temperature (T_c) of Y–Ba–Cu–O superconductor (T_c, end point) was 90 K and its critical current density (J_c) was above 230 A/cm^2 (at 77 K). The T_c value of sintered Bi–Pb–Sr–Ca–Cu–O body was increased from 55 K to 103 K, because the low-T phase was converted to high-T phase by the long heat treatment. The optimum J_c value of Bi–Pb–Sr–Ca–Cu–O sintered body was 172 A/cm^2 (at 77 K).

Introduction

There are many problems to be solved before oxide superconductors can be applied as polycrystalline bulk material. They include control of the microstructure and improvement of formability to complicated shape without deterioration of the microstructure. Superplastic deformation is a desirable property since it assists in forming ceramics of complicated shape. The superplastic phenomenon is closely related to submicron grain size in the densely sintered body. Yet the superconducting properties are improved by decreasing the grain boundaries, which results in a microstructure with bigger grains in the sintered body.

An oxide superconductor consists of many elements, and it is very difficult to prepare a superconductive powder having a homogeneous distribution of elements. Such a distribution in particles, and the particle size as well, are truly dependent on the synthesizing technique. The alkoxide method is a well-known technique by which we can prepare very fine powder with a homogeneous distribution of elements. But this technique has two disadvantages: (1) it is very difficult to prepare a wholly mixed sol of several elements; and (2) the cost of metal alkoxide is high.

As to ease of control of quantitative composition and of the morphology of the prepared particles, the mist pyrolysis method is excellent for multicomponent systems like oxide superconductors. Kodas et al. synthesized Y–Ba–Cu–O superconducting particles by this method. Tohge et al. succeeded in preparing superconducting particles of a Bi-system superconductor directly by control of the reaction atmosphere. Tohge et al. controlled particle morphology in a Bi-system superconductor by control of the temperature profile in the reactor.

Superconducting properties of bulk body obtained by using synthesized powders depend on the sintering property of the powder. An evaluation of the powder preparation, sinterability, and superconductivity is therefore required for utilization of mist-pyrolyzed powder. We have reported the synthesis of homogeneous Y–Ba–Cu–O powder by the mist pyrolysis method. Additionally, the sinterability of Y–Ba–Cu–O powder of submicron grain size was examined for powder obtained by the spray-drying method. In this case, the sintered density saturated less than 95% at relatively lower sintering temperature to depress abrupt grain growth. It is of interest to clarify the sintering and superconducting properties of powder synthesized by the mist pyrolysis method because of its high quality as a raw powder for sintering.

In this paper, synthesis of oxide superconductors (Y–Ba–Cu–O and Bi–Pb–Sr–Ca–Cu–O systems) by the mist pyrolysis method and the sinterability and superconductivity of the resulting powders are discussed. In the case of Y–Ba–Cu–O superconductor, superconducting particles with diameters of 0.05–1.0 μm were directly synthesized, and these
particles were a so-called "123" compound. The crystallinity and morphology of the particles were easily controlled by control of reaction temperature, reaction time and solution concentration. In the case of Bi-Pb-Sr-Ca-Cu-O superconductor, so called "low-\(T_C\) phase" powder was synthesized directly and this phase was turned into "high-\(T_C\) phase" through prolonged post-annealing. Dense, polycrystalline bulk bodies of Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O superconductors were fabricated by sintering the powders obtained, and they showed good superconducting properties as polycrystalline body.

**Experimental Procedure**

The starting solutions for Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O were prepared by dissolving nitrates of the elements. These solutions were nebulized by ultrasonic vibrator (frequency: 4MHz). The molar ratio in Y-Ba-Cu-O oxide was \(Y:Ba:Cu = 1:2:3\), and in Bi-Pb-Sr-Ca-Cu-O oxide it was \(Bi: Pb: Sr: Ca: Cu = 1.84: 0.34: 1.97: 2.03: 3.06\). Atomicized droplets of starting solution were carried by oxygen or argon gas to the reaction zone, which was held at planned temperatures. The reaction temperature ranged within 700–1100°C in preparing Y-Ba-Cu-O and within 650–750°C in preparing Bi-Pb-Sr-Ca-Cu-O. The reaction zones were 100 mm in length and 36 mm ID for Y-Ba-Cu-O and 650 mm in length and 36 mm ID for Bi-Pb-Sr-Ca-Cu-O. The flow rate of carrier gas varied from 0.6 to 2.0 l/min for Y-Ba-Cu-O and from 0.2 to 4.0 l/min for Bi-Pb-Sr-Ca-Cu-O. The corresponding residence times of atomicized droplets in the reaction zone were 3–10s and 10–200s respectively. The resulting particles were collected by filtration, using a PTFE filter with a pore size of 0.2 \(\mu\)m. Experimental conditions are listed in Table 1.

The powders obtained were examined by X-ray diffraction, scanning electron microscopy (SEM) and analytical electron microscopy (AEM). The superconductivity of as-pyrolyzed powder was evaluated in terms of magnetization related to temperature by a vibrating sample magnetometer (VSM). The density of sintered body was measured by the Archimedes method. The temperature dependence of resistivity and critical current density of superconductive oxide were measured by the four-probe method.

**Results and Discussion**

1 **Synthesis Process**

1.1 **Synthesis of Y-Ba-Cu-O phase**

A schematic diagram of the mist pyrolysis method is shown in Fig. 1. Droplets generated from the starting solution were dried and crystallized in the reaction zone. Thus morphology of resulting particles was affected by the initial condition of the solution, especially the solution concentration. The crystallinity depended on reaction conditions, that is, temperature, reaction time, atmosphere during the reaction and the kind of solution-such as nitrates, acetates or alkoxides.

Figure 2 shows the relationship between crystalline phase and reaction temperature. Reaction time was controlled by amount of carrier gas and length of reaction zone. In this case, the amount of carrier gas was set at 0.9 l/min and the reaction time was within 10 s. Intermediate phases in this system, that is, Ba(NO\(_3\))\(_2\), BaCO\(_3\), Y\(_2\)O\(_3\), CuO, BaCuO\(_2\) and Y\(_2\)Cu\(_2\)O\(_5\), were crystallized at 700°C, and crystallization of superconductive phase began in the reaction at 800°C. Powder of superconductive phase was obtained in the reaction at 950–1000°C; above this optimum temperature, superconducting phase was partially decomposed. In the solid-state reaction, superconducting phase was obtained by reaction at 900–950°C. In the liquid-phase reaction, the oxalate coprecipitation method, for example, a reaction temperature in the range of 800—850°C and a reaction time of a few hours in this temperature range was enough to prepare the superconducting phase. In our mist pyrolysis method the crystallization of superconductive phase was completed in a short reaction time, because the elements Y, Ba and Cu were mixed homogeneously in the starting solution and the small size of the droplets allowed quick heating.

The atmospheric gas affected the pyrolysis of mists and crystallization of pyrolyzed particles. In the
oxygen atmosphere, the amount of carrier gas had no influence on crystallinity. In the atmosphere of argon gas at 1 atm, the synthetic reaction of the superconductive phase was hindered (Fig. 3(a)). To promote the synthesis reaction of the superconductive phase, the partial pressure of oxygen gas was crucial.

To improve magnetic flux pinning property, some kinds of secondary phase were added as composite materials by various methods.\textsuperscript{1,16} In the case of mist pyrolysis, crystallization of superconducting phase was not affected by the addition of Ag as Ag(NO\textsubscript{3})\textsubscript{2} solution (15 mol\% to Y-Ba-Cu-O), but the addition of Si (5 mol\%) as silicon ethoxide prevented it at same reaction condition (Fig. 3(b) and (c)). This fact suggested that some kind of equilibrium reaction was not reached in the short reaction time.

The particle size of pyrolyzed powder depends on the diameter of nebulized droplets, which depends on the solution concentration and the exciting ultrasonic frequency.\textsuperscript{9,10} Figure 4(a) shows the relationship between solution concentration and diameter distribution of pyrolyzed particles. With decreasing concentration of the solution, average particle size and its distribution decreased. The morphology of the pyrolyzed powder is shown in Fig. 4(b). SEM photograph of powder of superconductor showed submicron (particle diameter about 0.05–0.2 \( \mu \)m) and well isolated state for each particle in the case of the solution concentration of 0.0005 mol/l. The TEM photographs indicate the well-dispersed state of each particle and the twin-domain structure in each particle that was derived from phase transition from the tetragonal phase to the orthorhombic in the as-prepared powder. This result indicated superconductivity in each particle. No particles were observed with porous structure, which is related to the solution and pyrolysis conditions.\textsuperscript{14} The compositional distribution of each particle on the compositional triangle diagram show the coincidence of molar ratio with superconducting (\( 1:2:3 \)) phase (Fig. 5(a) and (b)).
Well-crystallized particles converted from the tetragonal phase to the orthorhombic phase should have superconductivity. Their superconductivity depends on the amount of oxygen defects. Magnetization measurement of the powder at a temperature lower than $T_C$ is suitable for the evaluation of superconductivity in as-prepared state. Figure 6 shows the relationship between magnetization and temperature of as-prepared powder. The powder with average particle size of 0.5 $\mu$m filled the sample holder with a density of 1.46 g/cm$^3$. The magnetization (Meissner) signal that was detected under 90 K increased with decreasing temperature and showed a change of slope of curve at around 80 K. This gradual increase of magnetization may derived from superconductivity of the powder and the effect of the length of London penetration depth relative to particle size. Well-crystallized as-prepared particles showed superconductivity of $T_C$ (onset) = 90 K.

1.2 Synthesis of Bi-Pb-Sr-Ca-Cu-O superconducting phase

Bi-Pb-Sr-Ca-Cu-O superconductor was also prepared by the mist pyrolysis method. The reaction temperature for Bi-Pb-Sr-Ca-Cu-O was about 300°C lower than that for Y-Ba-Cu-O. The reaction time for Bi-Pb-Sr-Ca-Cu-O, on the other hand, was longer than that for Y-Ba-Cu-O. Figure 7(a) and (b) shows the relationship between crystalline phase and each reaction condition. It requires dozens and hundreds of hours to prepare the Bi-Pb-Sr-Ca-Cu-O superconducting high-$T_C$ phase by the solid-state reaction. To prepare the powder with high-$T_C$ phase the residence time in the reaction zone was controlled in the range of 10–200 s by the amount of carrier gas. But the prepared powder of submicron diameter had not the high-$T_C$ phase but rather the low-$T_C$ phase (Fig. 8 and Fig. 9(a)). This result indicates that the crystallization of high-$T_C$ phase was not promoted by decreasing the atomic diffusion distance on the order of particle size. The probability of the contribution of activation energy for the crystallization of high-$T_C$ phase through low-$T_C$ phase was also suggested. Crystallization of high-$T_C$ phase is probably difficult in a short reaction time in the mist pyrolysis method because of its complicated crystal structure. Decrease in particle size which resulted from decreasing the solution concentration to enhance the reaction caused the vaporization of volatile Bi- and Pb-components (see Fig. 9(b)). The powder with low-$T_C$ phase was turned to high-$T_C$ phase through prolonged annealing at a temperature above the partial melting temperature (at 850°C for
2 Sintering and Superconducting Properties

2.1 Sintering process and superconductivity of Y–Ba–Cu–O

Oxide superconductors have the feature on its grain growth mode. Their sintering temperatures are close to or the same as their partial melting temperatures. Thus the optimum sintering temperature range is narrow. Figures 10 and 11 show the relationship between the sintering temperature, time and the bulk density and grain size for Y–Ba–Cu–O compacted bodies made from the mist-pyrolyzed powder. Bulk density was close to theoretical density at 920°C to 930°C, but partial melting (mainly occurrence of Cu-rich phase) occurred about 920°C. The optimum sintering temperature of coarse powder derived by the solid-state reaction method was about 950–980°C. The reason for this decrease in optimum sintering temperature is considered to be that the powder sinterability is improved by decreasing the particle size and by greater homogeneity. The microstructure of the bodies sintered above 900°C showed significant grain growth. The X-ray diffraction pattern of the sintered body obtained at the optimum sintering temperature showed pure and well-crystallized superconducting phase (Fig. 11(b)).

The superconducting transport current property of sintered body is affected by the character of both the quality of each superconducting grain and the grain boundary structure. This transport property of oxide superconductor having short coherent length is affected not only by impurity phase in the grain boundaries but also by the misorientation angle at yet “clean” grain boundaries. The reason for differences in R–T curves of each sintered body (Fig. 12) was considered to be that the grain linkage structures of the superconducting grain in sintered bodies were different from one another. Sintered bodies except that sintered at 930°C were composed of Y–Ba–Cu–O single phase. The specimen sintered at 860°C showed the semiconducting feature of resistivity to decreasing temperature and had a long tail on reaching $T_c$, which was about 30 K. The tail remained in the specimen sintered at 880°C. The specimen sintered about 900°C showed a $T_c$ of around 90 K and had a short transition temperature range.

From the result of microstructure observation, it
was clear that the grain boundaries were reduced by grain growth. This fact is very important in regard to the superconducting transport current property. Figure 13 shows high-resolution images of sintered body obtained at 920°C for 10 h. Most of the grain boundaries showed a sharp boundary structure without a segregation phase but with some misorientation (Fig. 13(A)). A small amount of segregating phase at some grain boundaries and a distorted region along grain boundaries were observed (Fig. 13(B)). A weak linkage was deduced from this photograph. Evaluation of a real transport path and grain boundary observation must be done totally, although a tendency of reconciliation of grain linkage state with transport property was revealed in this experiment. The maximum critical current density \( J_c \) value obtained for the optimum sintered body was 230 A/cm². Elimination of the grain boundary is further expected to improve transport current.

2.2 Sintering process and superconductivity of Bi-Pb-Sr-Ca-Cu-O

Grain growth of Bi-Pb-Sr-Ca-Cu-O superconductor is significantly anisotropic because of its layered crystal structure. Intermediate pressing or hot pressing is effective for grain orientation.

Compact body made from obtained powder consisting of low-\( T_c \) phase (the chemical composition of high-\( T_c \) phase) sintered at 840–850°C (below partial melting temperature) for 10–80 h at low oxygen partial pressure. High-\( T_c \) phase was crystallized as almost single phase by sintering for 40–80 h. The sintering process had not been coupled with any grain-orientating process. Conversion from low-\( T_c \) phase to high-\( T_c \) phase and enhancement of grain linkage improved the superconductivity (Fig. 14). Prolonged sintering enhanced the R-T property. Maximum \( T_c \) and \( J_c \) values were 103 K and 172 A/cm², respectively.

The microstructure of the sintered body obtained at the above temperature for 80 h (Fig. 15(A) and (B)) showed orientation of tabular grains. This orientation was suitable for superconducting current path (parallel to c-plane). A high-resolution image of the many grain boundaries showed "clean" grain boundary (Fig. 15(C)).

Conclusion

(1) Superconducting fine powder of Y–Ba–Cu–O single phase was synthesized by the mist pyrolysis method. Obtained particles were dispersed well and their particle size was controlled by the change of solution concentration. The powder obtained by the reaction at 950–1000°C was crystallized as the superconducting orthorhombic phase. The size of obtained particles was controlled to the order of less than 0.1 μm in diameter. (2) As-mist pyrolyzed particles had superconductivity. The compacted body was sintered at 900–920°C. The sintered body had a bulk density of above 90% of theoretical density. Grain growth occurred significantly above 900°C. Sintered body had \( T_c \) value of 90 K and \( J_c = 230 \) A/cm². Superconducting grains were combined tightly with one another. (3) Bi-Pb-Sr-Ca-Cu-O superconducting (low-\( T_c \) phase) powder of submicron size was synthesized at near 700°C. The
optimum flow rate of Ar and the optimum solution concentration were adopted. The chemical composition of the solution was equal to that of high-$T_C$ phase. (4) Obtained powder of low-$T_C$ phase was converted to high-$T_C$ phase by long heat treatment. The superconducting transport current of sintered body of Bi–Pb–Sr–Ca–Cu–O superconductor was affected by the sintering condition. The $T_C$ value at optimum condition was 103 K and the $J_C$ value was 172 A/cm$^2$.

Literature Cited