Synthesis of TiO₂-Ag Composite Powder by Spray Pyrolysis

Mineaki MATSUMOTO, Kenji KANEKO, Yoshiyuki YASUTOMI, Satoshi OHARA,
Takehisa FUKUI and Yasuo OZAWA*

Research and Development Laboratory, Japan Fine Ceramics Center (JFCC), 2-4-1, Mutsuno, Atsuta-ku, Nagoya-shi 456-8587
*Engineering Research Association for Superconductive Generation Equipment and Material (Super-GM),
5-14-10, Nishi-Tenma, Kita-ku, Osaka-shi 530-0047

噴霧熱分解法による TiO₂-Ag 複合粒子の合成

松本峰明・金子賢治・安富義幸・大原 智・福井武久・小沢保夫*

(財)ファインセラミックスセンター, 456-8587 名古屋市熱田区六野 2-4-1
*超電導発電関連機器・材料技術研究組合, 530-0047 大阪市北区西天満 5-14-10

Spray pyrolysis was used to fabricate TiO₂-Ag composite powders for application in oxide barrier between filaments of superconducting multifilamentary tapes. The powders were prepared from an aqueous solution of TiO₂ sol and AgNO₃. SEM and TEM observations revealed that the average size of the synthesized powder was less than 1 μm and consisted of well-dispersed fine primary particles of TiO₂ and Ag. It was clearly observed that the microstructure of the particles was altered by conditions of heat treatment.

[Received July 25, 2001; Accepted October 17, 2001]

Key-words: Spray pyrolysis, Composite powder, Superconducting tape, Oxide barrier

1. Introduction

Spray pyrolysis has advantages in preparing composite powders with controlled morphology, phase composition and size distribution. It is considered as a useful method to fabricate starting powders of composite materials with advanced and additional properties.¹⁾ Ceramic composite powders synthesized by spray pyrolysis are often used to fabricate composite ceramics with improved mechanical and electronic properties.²⁾⁻⁵⁾ Synthesis of metal composite powders and metal-ceramic composite powders by spray pyrolysis has been also applied to design materials with additional properties.⁶⁾⁻¹⁰⁾

Low AC loss of multifilamentary superconducting tapes and wires are required for applications of high T_c materials used in the situation of alternating currents and fields. Recently, Flükiger et al. reported that surrounding each filament with a layer of oxide (called "barrier") made it possible to reduce AC loss significantly in Ag-sheathed Bi(2223) multifilamentary tapes.^{11),12)} The role of the oxide barrier is to increase the transverse resistivity between filaments as well as to inhibit the "bridging effect" in which Bi(2223) grains grow out of the filament and directly connect the other filaments.^{11),12)}

The fabrication of the superconducting tapes with oxide barrier long enough for practical use has not been achieved due to the difficulty of homogeneous introduction of the oxide barrier in the tapes after drawing or swaging. The heterogeneous formation of the oxide barrier decreases the workability of the tape and yields strong sausaging of the filament.¹¹⁾ One of the solutions to these problems is considered to use Ag-oxide composite powder as the starting powder of the oxide barrier because the metal-ceramic composite powder must have an ability of deformation during drawing or swaging, which make it possible to form the barrier uniformly. The use of the Ag-oxide composite would also lead to the good adhesion of the barrier to Ag matrix, which will make good effects on preparing long tapes and reducing AC loss.

TiO₂ is one of the candidates for barrier material of Bi-based superconducting tapes since TiO₂ does not react with Ag or Bi(2223) phase.

The aim of our work is to fabricate high performance Bi-based superconducting barrier tapes by using Ag-oxide composite powder as the starting material of the barrier.

In this paper, synthesis of TiO₂-Ag composite powder and the effect of processing conditions on microstructure evolution of the powder will be discussed as a first step of our study.

2. Experimental procedure

TiO₂ sol (C. I. Kasei, purity > 99.8%, mean particle size: 50 nm) and AgNO₃ (Kojundo Chemical Laboratory, purity > 99%) were used as the starting materials. These materials were dissolved in distilled water to obtain 0.1 mol/l of the solution. The molar ratio of TiO₂ and Ag in the solution was kept 3:1. The solution was atomized with an ultrasonic vibrator operated at 1.7 MHz. Droplets were introduced into a horizontal reaction furnace with argon as a carrier gas (flow rate: 3 L/min). Details about the apparatus are given elsewhere.³⁾ The reaction furnace had four heating zones, and four types of the temperature profiles in the temperature zones were selected as shown in Table 1.

Morphology of synthesized powders was observed by a scanning electron microscopy (SEM; Hitachi, S-4500). The particle size distribution was determined by a laser particle analyzer (Malvern, Master Sizer). The phases were analyzed by X-ray diffraction (XRD; Philips, PW1877). A transmission electron microscope (TEM; JEOL, JEM2010) equipped with energy dispersive X-ray spectrometer (EDS)

Table 1. Conditions of Heat Treatment for Each Sample

Sample	Temperature in the heating zone			
	Zone 1	Zone 2	Zone 3	Zone 4
1	200°C	500°C	500°C	500°C
2	200°C	500°C	700°C	900°C
3	200°C	500°C	700°C	1000°C

was also employed to investigate microstructure of the powders. TEM samples were prepared by embedding the particles into epoxy resin and then cutting into thin sections (thickness: about 70 to 80 nm) with microtome (LKB, LKB4800).

3. Results and discussion

Figure 1 presents a typical XRD pattern from sample 1. It is clear that the powder are consisted of Ag and TiO_2 (the crystalline phases are mixture of rutile and anatase). It was confirmed that the other samples were made of Ag and TiO_2 as sample 1.

Figure 2 exhibits an SEM image of sample 1. The synthesized particles were spherical as shown in Fig. 2, and the difference of morphology among samples was minor. Laser analysis revealed that the mean particle size of each sample was 0.6–0.7 μm and the size distribution of each powder is very narrow (Fig. 3).

In order to investigate microstructure of the powders in detail, TEM observations of the particles were carried out as shown in Fig. 4. TEM-EDS analysis clarified that strongly contrasted particles in the composite powder were Ag, and weakly contrasted particles were TiO_2 . As shown in Fig. 4 and Fig. 5, fine spherical Ag particles (less than 20 nm) are uniformly dispersed on the surface of the TiO_2 grains of about 50 nm for sample 1. In the case of sample 2, Ag particles are also well dispersed although the Ag particles become larger than those of sample 1. On the contrary, the state of distribution of sample 3 obviously altered.

Fig. 1. XRD pattern of sample 1.

Namely, the Ag particle becomes much larger than those of other samples and some of them link together without marked growth of TiO_2 grain. The Ag particles are not uniformly dispersed and seem to aggregate into the interior of the powder. To make clear the structural change of the powder, the composite powder of higher Ag content (TiO_2 -

Fig. 2. SEM image of sample 1.

Fig. 3. Mean size and distribution of each sample.

Fig. 4. TEM photographs of the synthesized powders; a) sample 1, b) sample 2 and c) sample 3.

Fig. 5. High resolution image of sample 1.

Fig. 6. Microstructure of TiO_2 -50 mol%Ag composite powder.

50 mol%Ag) were prepared. Figure 6 shows a TEM image of the Ag-rich composite powder synthesized at the same condition of sample 3. The Ag-rich composite has the microstructure in which a large inner Ag particle is encapsulated by TiO_2 particles. It is speculated that the rearrangement of well-dispersed primary particles of Ag and TiO_2 took place during the processing to form the "capsule-type" composite powder in which Ag condenses into the interior of the composite powder.

Similar phenomena of the rearrangement of constituents in composite powders are reported for other systems.^{8),13)} Arami et al. found that well-dispersed Cu- Al_2O_3 composite powder became Cu encapsulated Al_2O_3 powder at high temperature due to the poor wettability of Cu on Al_2O_3 .¹³⁾ Che et al. reported that dispersed Pd aggregated into the interior of SiO_2 -Pd composite powder during heat treatment, and the reason of the rearrangement was considered due to the

difference of surface free energy between the constituents.⁸⁾ In both cases, it was thought that the rearrangement of primary particles would lead to an overall decrease in the energy of the systems.

In the case of Ag- TiO_2 , the reason of microstructural change would be attributed to the melting of Ag during the processing. Because of the melting point of Ag (about 960°C), Ag become liquefied during the preparation of sample 3, and aggregates into the interior of the composite powder.

Experimental study revealed that the contact angle of liquid Ag on sintered TiO_2 is about 120° at 1000°C in argon atmosphere, showing that the wetting behavior of Ag on TiO_2 is not good. It is concluded that the poor wettability of Ag on TiO_2 results in coarsening Ag in the composite particle above the melting point of Ag.

4. Conclusion

TiO_2 -25 mol%Ag composite powders were successfully synthesized by ultrasonic spray pyrolysis from the solution of TiO_2 sol and AgNO_3 . The synthesized powders were spherical and the mean particle size is less than 1 μm . In the case of syntheses below the temperature of the melting point of Ag, the composite powder is consisted of well-dispersed fine particles of Ag and TiO_2 . On the contrary, when synthesized above the melting point of Ag, the Ag particles became large and tend to aggregate into the interior of the composite powder. In future work, we will apply these TiO_2 -Ag composite particles to fabricate the superconducting tapes with oxide barrier.

Acknowledgement This work has been carried out as a part of Super-ACE (R & D of fundamental technologies for superconducting AC power equipment) project of METI, being consigned by NEDO.

References

- 1) Messing, G. L., Zhang, S. C. and Jayanthi, G. V., *J. Am. Ceram. Soc.*, **76**, 2707-26 (1993).
- 2) Suzuki, T., Itatani, K., Aizawa, M., Howell, F. S. and Kishio, A., *J. Eur. Ceram. Soc.*, **16**, 1171-78 (1996).
- 3) Fukui, T., Oobuchi, T., Ikuhara, Y., Ohara, S. and Kodera, K., *J. Am. Ceram. Soc.*, **80**, 261-63 (1997).
- 4) Fukui, T., Ohara, S. and Mukai, K., *Electrochemical and Solid-State Letters*, **1**, 120-22 (1998).
- 5) Maric, R., Fukui, T., Ohara, S., Yoshida, H., Nishimura, M., Inagaki, T. and Miura, K., *J. Mater. Sci.*, **35**, 1397-404 (2000).
- 6) Pluym, T. C., Kodas, T. T., Wang, L. M. and Glicksman, H. D., *J. Mater. Res.*, **10**, 1661-73 (1995).
- 7) Okuda, A., Watanabe, K., Sakakushi, S., Taneiti, K., Watanabe, Y., Shiota, S. and Shibata, J., *Shigen to Sozai*, **116**, 527-31 (2000) [in Japanese].
- 8) Che, S., Sakurai, O., Shinozaki, K. and Mizutani, N., *J. Ceram. Soc. Japan*, **104**, 38-43 (1996) [in Japanese].
- 9) Carim, A. H., Dougherty, P., Kodas, T. T. and Ott, K., *Mater. Lett.*, **8**, 335-39 (1989).
- 10) Kobayashi, N., Matsuda, H. and Hasatani, M., *Kagaku Kougaku Ronbunshu*, **18**, 371-75 (1992) [in Japanese].
- 11) Huang, Y. B. and Flükiger, R., *Physica C*, **291**, 71-82 (1998).
- 12) Huang, Y. B., Dhalle, M., Witz, G., Marti, F., Giannini, E., Walker, E., Passerini, R., Polcari, A., Clerc, S., Kwasnitza, K. and Flükiger, R., *J. Superconductivity*, **11**, 495-504 (1998).
- 13) Arami, Y., Korekawa, H. and Iwatsu, O., *J. Japan Soc. Powder Powder Metall.*, **34**, 264-68 (1987) [in Japanese].