JOURNAL OF MATERIALS SCIENCE 26 (1991) 6275–6278

Preparation and characterization of $YBa_2Cu_3O_{7-x}$ powder by the ultrasonic spray pyrolysis method

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A single-phase $YBa_2Cu_3O_{7-x}$ powder was prepared in an air flow system by thermally decomposing droplets containing the nitrate salts of yttrium, barium and copper in distilled water. The powder obtained had a mean particle size 0.78 μm and a very narrow particle size distribution. The total porosity of the powder was estimated to be about 63%. It was found that much agglomeration had occurred among the droplets, which would have an adverse effect on the particle size distribution. The bulk density of a sintered specimen using the powder prepared at 950 °C was higher than 97% theoretical density.

1. Introduction

The low critical current density, J_c, of a $YBa_2Cu_3O_{7-x}$ sintered body restricts its practical applications. The J_c value of $YBa_2Cu_3O_{7-x}$ sintered body prepared by the conventional mixed oxide method is about 150 to 600 A cm^{-2} [1], which is far less than those of epitaxially grown thin films (10^4–10^5 A cm^{-2}) [2] and the bulk specimen prepared by the melt-texture growth method (about 7400 A cm^{-2}) [1]. This discrepancy may be due to the structural discontinuity [3] or the presence of $BaCO_3$ and second phases at the grain boundaries [4], which restricts the transport of current across the grain boundary [3]. As Alford *et al.* [5] have shown that the J_c value of $YBa_2Cu_3O_{7-x}$ is proportional to its density, this discrepancy may also come from the low density of $YBa_2Cu_3O_{7-x}$ sintered body through the conventional mixed oxide method. Therefore, a $YBa_2Cu_3O_{7-x}$ sintered body with high density and free from $BaCO_3$ and second phases, should be prepared to achieve high J_c value. However, the conventional mixed oxide method is inadequate for this purpose because the generation of chemical inhomogeneity and hard agglomerates is seldom avoided in this process.

The ultrasonic spray pyrolysis (USP) method is a recently developed and very promising technique to prepare fine, agglomerate-free, and homogeneous oxide powders [6–8]. Recent work [9–12] has shown that a fine and homogeneous $YBa_2Cu_3O_{7-x}$ powder can be synthesized using this process. However, there has been no attempt to make a dense $YBa_2Cu_3O_{7-x}$ body using this process, and powder characteristics, which are critical to the sinterability, have not been investigated. In this study, characteristics of $YBa_2Cu_3O_{7-x}$ powder prepared by the USP method are investigated and a dense sintered body has been made using this powder.

2. Experimental procedure

Fig. 1 shows a schematic diagram of the apparatus for powder preparation. An aqueous solution of $Y(NO_3)_3\ 5H_2O$, $Ba(NO_3)_2$, and $Cu(NO_3)_2\ 3H_2O$ in a 1:2:3 molar ratio and 0.05 mol l^{-1} overall concentration was prepared. The mist of this solution, which was generated by an ultrasonic atomizer, was decomposed in a furnace in the temperature range 800–1100 °C. Air or nitrogen gas was used as a carrier gas at a flow rate of 6 l min^{-1}. The average dwell time of droplets in the furnace was estimated to be ~ 10 s.

The powder produced was analysed by X-ray diffraction (XRD) and thermogravimetry (TG). It was also characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The specific surface area and specific gravity of this powder were measured by the BET and pycnometer methods, respectively.

The powder prepared at 950 °C with air as carrier gas was sintered at 950 °C for 6 h and annealed at 500 °C for 12 h in an oxygen atmosphere. The microstructure of the sintered specimen was observed by reflecting polarized optical microscopy and its electrical property was measured by the four-point probe method.

3. Results and discussion

3.1. Formation of $YBa_2Cu_3O_{7-x}$ single-phase powder

XRD results show that $YBa_2Cu_3O_{7-x}$ single phase can be obtained in the temperature range 900–1000 °C when air is used as a carrier gas. However, $BaCO_3$ was detected in the powder prepared below 900 °C and non-superconducting phases were found in the powder synthesized above 1000 °C. In the case of nitrogen carrier gas, non-superconducting phases were detected

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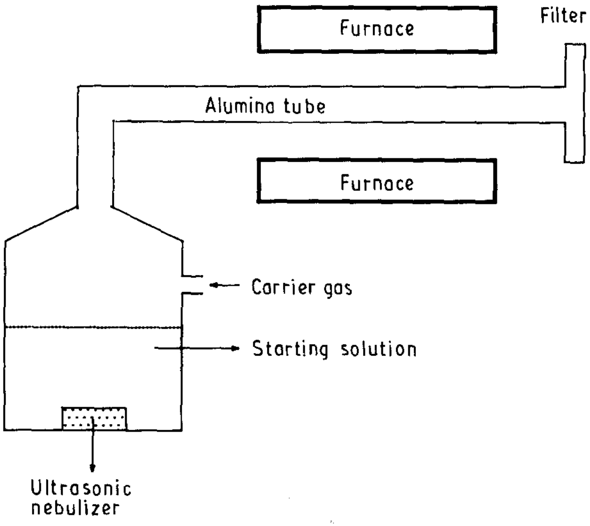

Figure 1 A schematic diagram of the experimental apparatus.

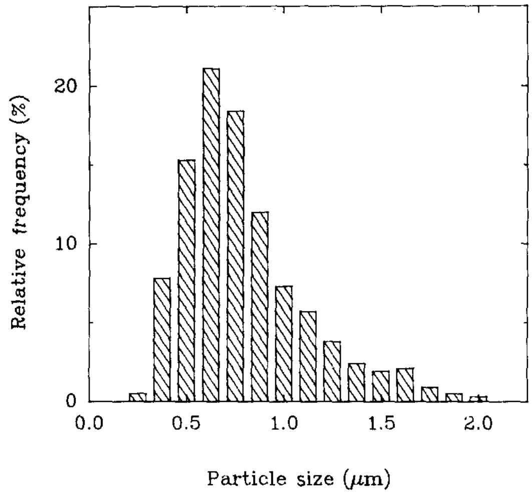

Figure 2 The particle-size distribution of $YBa_2Cu_3O_{7-x}$ powder prepared at 950 °C using air as carrier gas.

even in the powder prepared at a temperature as low as 900 °C. Diffraction lines of the powders synthesized with nitrogen carrier gas were rather broad and had much lower intensities than those of the powders prepared with air carrier gas. In this work, nitrogen was used as a carrier gas to avoid the formation of $BaCO_3$ because the presence of $BaCO_3$ is detrimental [4] to superconducting properties of $YBa_2Cu_3O_{7-x}$. However, a powder with $YBa_2Cu_3O_{7-x}$ single phase could not be prepared, despite the absence of $BaCO_3$. This might be due to the fact that nitrate salts could not be fully decomposed owing to the lack of oxygen, which was confirmed by comparing the weight loss of each powder measured by TG. Powders prepared at 1000 °C with nitrogen carrier gas and at 950 °C with air carrier gas show 4.5% and 2.1% weight loss, respectively, when they were heated to 950 °C in an oxygen atmosphere. Therefore, it was concluded that the droplets should be decomposed between 900 and 1000 °C in an oxygenating atmosphere to obtain the single-phase $YBa_2Cu_3O_{7-x}$ powder.

3.2. Particle-size distribution of $YBa_2Cu_3O_{7-x}$ powder

Fig. 2 shows the particle-size distribution of the powder prepared at 950 °C with air carrier gas, where the maximum diameters of more than 500 particles were measured on the scanning electron micrographs. The average particle size is 0.78 μm and the standard deviation, $\sigma_n (\sigma_n = 1 + \sigma/d$ [13], where d is the average particle size), is 1.41, respectively. The particle-size distribution of $YBa_2Cu_3O_{7-x}$ powder synthesized by the USP method has been seldom reported. ZnO powder prepared by the USP method using $Zn(CH_3COOH)_2\,2H_2O$ as the starting material [8] has shown approximately the same distribution because σ_n was 1.5 in this case. However, the $YBa_2Cu_3O_{7-x}$ powder synthesized by oxalate coprecipitation had a broader distribution ($\sigma_n = 1.7$) than our powder, even though its average particle size was smaller ($d = 0.5$ μm).

The mean size of atomized liquid droplets can be determined from the equation [14]

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

where γ is the surface tension of the solution, ρ is the specific gravity of the solution, and f is the frequency of the ultrasonic nebulizer. Here γ and ρ can be assumed to be equal to the values of the pure distilled water because the solution is very dilute. If $\gamma = 75.1$ dyn cm^{-1}, $\rho = 1.0$ g cm^{-3}, and $f = 1.8$ MHz, the droplet size, d_{drop}, is calculated to be 2.8 μm from Equation 1. Assuming one $YBa_2Cu_3O_{7-x}$ dense particle is derived from one droplet, the mean diameter of dense $YBa_2Cu_3O_{7-x}$ particles can be calculated using the following equation:

$$d_{1-2-3} = \left(\frac{CW}{1000D}\right)^{1/3} d_{\text{drop}} \quad (2)$$

where C is the concentration of solution, W is the molar weight of $YBa_2Cu_3O_{7-x}$, D is the theoretical density of $YBa_2Cu_3O_{7-x}$, and d_{drop} is the average diameter of droplets, respectively. We have modified the equation for the ZnO system suggested by Liu *et al.* [8] because it is not applicable to our system. The Equation 2 assumes that the starting material has been fully reacted to form $YBa_2Cu_3O_{7-x}$ phase. According to Equation 2, $d_{1-2-3} = 0.49$ μm was obtained when $C = 0.05$ mol l^{-1}, $W = 666.2$ g mol^{-1}, $D = 6.31$ g cm^{-3}, and $d_{\text{drop}} = 2.8$ μm.

Suppose that droplets are monosize, then the maximum and minimum particle sizes should be 2.8 and 0.49 μm, respectively. However, there were many particles smaller than 0.49 μm and larger than 2.8 μm, which indicates that the droplets have an unknown size distribution. This unknown size distribution will be one of the factors determining the size distribution of the generated particles. Further investigation is required on the size distribution of the droplets. Although it is not possible to produce monosize $YBa_2Cu_3O_{7-x}$ powders owing to the inherent size distribution of the droplets, $YBa_2Cu_3O_{7-x}$ powders with quite a narrower particle-size distribution can be obtained using the USP method than those prepared by the conventional or oxalate coprecipitation methods.

3.3. Estimation of powder porosity

The average particle size measured, 0.78 μm, is much bigger than the value calculated, 0.49 μm, using Equation 2. This discrepancy may be due to the formation of pores in some particles, as shown in Fig. 3. The formation of these inner pores must be one of the factors affecting the particle size and the distribution. However, few attempts have been made to estimate the inner porosity quantitatively. In this work, a method is suggested which can quantitatively estimate the inner porosity by measuring the particle size, the specific surface area, and the powder density.

Closed and open pores can be formed in the powder simultaneously. The closed porosity can be simply calculated by measuring the apparent density of the powder, which includes only the closed pores, using the pycnometer method. The closed porosity was estimated to be about 14% because the measured apparent density, $5.46\ \mathrm{g\,cm^{-3}}$, was 86.5% theoretical density. Now if the total porosity is known, the open porosity can be estimated just by subtracting the closed porosity from the total porosity. The total porosity can be determined by calculating the bulk density of the powder, which includes not only the closed pores but also the open pores, using the equation [15]

$$\rho = \frac{6}{dS} \tag{3}$$

where d is the average particle size and S is the specific surface area of the powder. If $d = 0.78\ \mu m$ and $S = 3.27\ \mathrm{m^2\,g^{-1}}$, the bulk density, ρ, is calculated as $2.35\ \mathrm{g\,cm^{-3}}$. The total porosity of the powder is about 63% because the bulk density is 37.2% theoretical density. Substrating the closed porosity, the powder has 49% open porosity. The generation of such highly porous particles might be due to the fact that the rapid evaporation of water from the surface of droplets formed a salt crust which prevented the still-trapped solution and gas from being expelled [7]. Further studies are required on the correlation between powder porosity and the sinterability of the powder because the change in powder porosity may cause a quite different sintering behaviour.

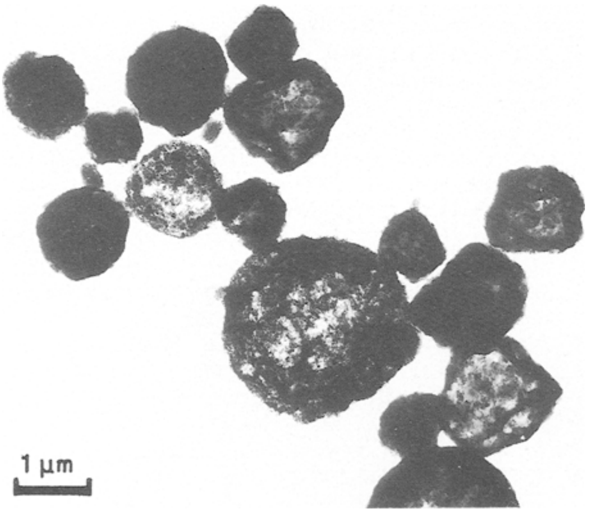

Figure 3 Transmission electron micrograph of $YBa_2Cu_3O_{7-x}$ powder, prepared at 950 °C using air as carrier gas, showing pores within the particle.

3.4. Agglomeration of the droplets

Some works on the USP method [7, 8] have been based on the assumption that one particle is generated from one liquid droplet. However, our results show that the assumption is not true. The average weight of particles with known average diameter can be simply calculated by multiplying their volume by their bulk density. With a measured average diameter of 0.78 μm and a density of $2.35\ \mathrm{g\,cm^{-3}}$ from Equation 3, the mean weight of particles is calculated to be 5.8×10^{-13} g. However, if one particle is generated from only one droplet, the average weight of particles is determined through a quite different calculation. Because the average diameter of droplets and the concentration of the solution are known, an equation is established as follows

$$\begin{aligned} M &= \frac{4}{3}\pi\left(\frac{10^{-4}d_{\mathrm{drop}}}{2}\right)^3\left(\frac{C}{1000}\right)W \\ &= 5.2 \times 10^{-16}CWd_{\mathrm{drop}}^3 \end{aligned} \tag{4}$$

where C is the concentration of the solution, W the molar weight of $YBa_2Cu_3O_{7-x}$, and d_{drop} is the average diameter of droplets. According to Equation 4, $M = 3.8 \times 10^{-13}$ g is obtained when $C = 0.05\ \mathrm{mol\,l^{-1}}$, $W = 666.2\ \mathrm{g\,mol^{-1}}$, and $d_{\mathrm{drop}} = 2.8\ \mu m$. Because this value, 3.8×10^{-13} g, is much smaller than 5.8×10^{-13} g, which is calculated from the measured particle size, it can be concluded that much agglomeration among liquid droplets has occurred. If the agglomeration takes place, the formation of bigger particles will be preferred, resulting in a broader particle size distribution. The asymmetry of particle-size distribution shown in Fig. 2 may be caused by this agglomeration.

3.5. Sintering behaviour

To obtain a $YBa_2Cu_3O_{7-x}$ sintered body with a high density using the powder prepared at 950 °C with air carrier gas, a suitable dispersing medium was chosen by the 5 day sedimentation method. Of the acetone, ethanol, methyl iso-butyl ketone (MIBK), and mixed solutions of ethanol and MIBK examined, the mixed solution of 80% ethanol and 20% MIBK was found to be the most suitable for dispersing $YBa_2Cu_3O_{7-x}$ powder. A green body, which was made by centrifugally casting the suspension prepared by dispersing the powder in the mixed solution, was sintered at 950 °C for 6 h and then annealed at 500 °C for 12 h. The heating and cooling rates were $300\ ^\circ\mathrm{C\,h^{-1}}$ and

$50\,^{\circ}\mathrm{C\,h^{-1}}$, respectively. All heat treatments were performed under 1 atm oxygen atmosphere. As shown in Fig. 4, the zero resistance temperature of the sintered specimen, measured by the four-point probe method, is 90 K. The bulk densities, measured by Archimedes method and the point counting method [16], were above 97% theoretical density.

It has been reported that, without liquid phase, the bulk density of the specimen prepared via the conventional mixed oxide route was only about 91% even if it had been sintered more than 24 h at 950 °C [4]. In Fig. 5, no liquid phase can be seen and an enormous grain growth is observed. Therefore, it is concluded that the powder synthesized in this study is much more reactive than a conventionally prepared powder so that a higher density of the sintered body can be achieved.

Although J_c of a $YBa_2Cu_3O_{7-x}$ sintered body was proportional to its bulk density, J_c decreased when the bulk density was too high owing to the difficulty of oxygen diffusion [5]. However, this oxygenating problem can be overcome by carrying out the annealing under very high oxygen pressure (about 20 MPa) [17]. With such an annealing process, the sintered body synthesized in this study would have a much higher J_c value than a conventionally prepared body.

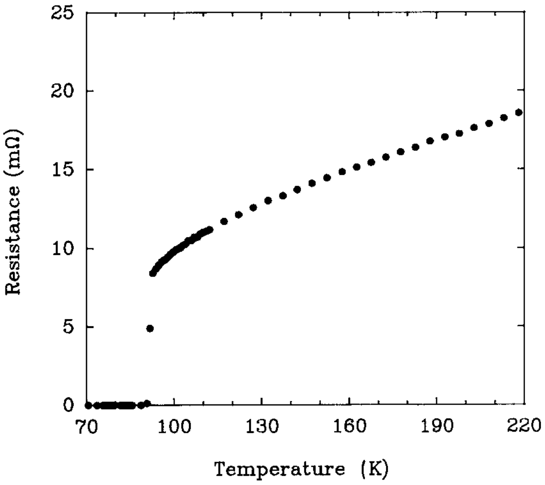

Figure 4 The electrical resistance as a function of temperature for a sintered $YBa_2Cu_3O_{7-x}$ sample.

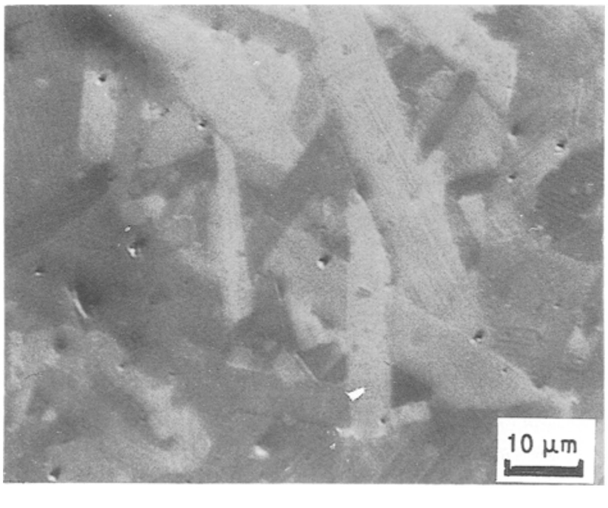

Figure 5 The optical micrograph of a sintered $YBa_2Cu_3O_{7-x}$ sample.

4. Conclusions

$YBa_2Cu_3O_{7-x}$ powder was synthesized by the ultrasonic spray pyrolysis method using mixed nitrates solution. Based on this study, the following conclusions can be drawn.

1. To obtain $YBa_2Cu_3O_{7-x}$ single-phase powder by the USP method, an oxygenating atmosphere and a pyrolysis temperature of 900–1000 °C are necessary.
2. The average particle size and the standard deviation of the powder were 0.78 μm and 1.41, respectively. The particle-size distribution was quite narrow.
3. The produced powder was very porous and a method to measure the porosity of the powder is proposed. Using this method, the total porosity of the powder, which would have a great effect on the sinterability, was estimated to be about 63% (closed and open porosity were 14% and 49%, respectively).
4. Contrary to the assumption for the USP method that one particle is generated from only one liquid droplet, much agglomeration among droplets has taken place, which might cause the tailing of the particle-size distribution to the larger side.
5. The bulk density of a sintered specimen using the powder prepared at 950 °C with air carrier gas was above 97% theoretical density, which is much higher than the value obtained by the conventional method.

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Received 23 August 1990
and accepted 28 February 1991