A comparison of the properties of Bi-2223 precursor powders synthesized by various methods

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Abstract

We report on the study of the (Bi,Pb) 2 Sr 2 Ca 2 Cu 3 O x precursor powders prepared by coprecipitation, citrate gel, and spray pyrolysis. All powders had the same starting nominal compositions, and were calcined under the same conditions. The properties of the precursor powders are compared. It is found that the phase compositions of these precursor powders are not identical, and the powder prepared by spray pyrolysis seems to be particularly different. Moreover, the observation of the Bi-2223 phase formation reveals that the spray pyrolysis powder transforms to Bi-2223 far faster than the other powders. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The development of HTS tapes using the Oxide Powder in Tube (OPIT) process has resulted in J c (77K, 0 T) of 7 × 10 4 A/cm 2 in short Bi-2223/Ag tapes [1]. Such encouraging values are only attained with very painstaking control of all processing parameters. The OPIT process involves the packing of a precursor powder into a silver alloy tube that is then subject to repeated mechanical deformation and heat-treatment steps. The precursor powder within the silver matrix undergoes conversion to the desired superconducting phase, the Bi-2223 phase, during the heat-treatment process. The three key parameters—powder processing, mechanical deformation, and heat treatment—determine the macrostructure and

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final physical properties of the tapes. The powder production stage, the first process in the production of OPIT tapes, is one of the most critical stages at it thereby influences the parameters that must be used in the later OPIT processing stages. Many studies covering HTS powder processing have been published [2,3]. A powder with phase composition of Bi-2212 as a major phase and some secondary phases is essentially suitable as a precursor [4]. The phase composition varies from powder to powder, depending on the starting nominal composition, the preparation method, and the calcination procedures. In this work, we study the properties of the Bi-2223 precursor powders prepared by different methods. All powders had the same starting nominal compositions and underwent the same heat treatment. The phase compositions in the precursor powders and the formation of the Bi-2223 phase will be discussed.

2. Experimental

Powders synthesized by coprecipitation, citrate gel, and spray pyrolysis were prepared from a mixed nitrate solution of Bi(NO$_3$)$_2$·5H$_2$O, Sr(NO$_3$)$_2$, Pb(NO$_3$)$_2$, Ca(NO$_3$)$_2$·4H$_2$O, and Cu(NO$_3$)$_2$·3H$_2$O, corresponding to the nominal composition, Bi$_{1.7}$Pb$_{0.4}$Sr$_{1.8}$Ca$_{2.2}$Cu$_{3.2}$O$_x$. The coprecipitation powder [5] was prepared by titrating the nitrate solution into a triethylenediamine/oxalic acid mix (ratio 1.8–2.2) with precipitation complete at a pH of 1. The precipitant was subsequently filtered and then dehydrated at 80°C for 24 h. This powder was then heated at 200°C for 2 h. The citrate gel [6] powder was prepared by first adding 1 g equivalent of citric acid (for each gram equivalent of metals) to the nitrate solution. The pH of this solution was further adjusted to 6 by adding ethylenediamine into the solution. The solution formed a gel at 100°C and subsequently heat treated at 200°C for 2 h. The spray pyrolysis powder was prepared by Merck KGaA in which the nitrate solution was sprayed as a fine, submicron mist into a heated reaction chamber. All of the powders were calcined together in air, first at 730°C for 24 h, then at 800°C for 48 h (with intermediate grinding every 24 h), and finally sintered at 842°C for 24 h (with intermediate grinding every 24 h).

X-ray powder diffraction (XRD) measurements were carried out with a SCINTAG (X1) diffractometer (Cu Kα radiation) and with a Siemens D5000 diffractometer. Energy dispersive X-ray Analysis (EDX) was performed using EDAX DX4. Elemental analyses were made using an Optima 3300XL ICP-optical emission spectrometer obtaining a relative standard deviation comparing against standard solutions of better than ±2%.

3. Results and discussion

The phases in the precursor powders change as both the calcination temperature and time increase. In Fig. 1, we show the XRD patterns of coprecipitation powders calcined at different temperatures. At 730°C, the Bi$_2$Sr$_2$CuO$_{6+x}$ (Bi-2201) phase is found to be the major phase. At 800°C, the diffraction peaks of Bi-2201 were seen to decrease in intensity as the calcination time increases, and those of the Bi$_2$Sr$_2$CaCu$_2$O$_x$ (Bi-2212) phase increase in intensity at the same time. After 48 h of calcination, Bi-2212 had become the major
crystalline phase. The $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Bi-2223) phase was detected after sintering at 842°C. Citrate gel and spray pyrolysis powders underwent similar phase development.

Fig. 2 shows the XRD patterns of the precursor powders calcined at 800°C for 48 h. The phase composition in each precursor is a mixture of the major phase Bi-2212 and some secondary phases, such as $\text{Ca}_2\text{PbO}_4$, $(\text{Pb,Bi})_3\text{Sr}_{3-x}\text{Ca}_{2+x}\text{CuO}_x$ (3321), and $\text{CuO}$. The $\text{Ca}_2\text{PbO}_4$ phase appears in all precursor powders, showing the diffraction peaks around $2\theta = 17.8°$, 18.3° and 32°. Compared to coprecipitation and citrate gel powders, the spray pyrolysis powder displays weaker $\text{Ca}_2\text{PbO}_4$ peaks, indicating that the spray pyrolysis powder contains less $\text{Ca}_2\text{PbO}_4$ than the other powders. This has also been examined quantitatively by comparing the intensities of the $\text{Ca}_2\text{PbO}_4$ peaks in all powders using the diffraction peak (115) of Bi-2212 in each powder as a reference. The $\text{CuO}$ phase, with diffraction peaks around $2\theta = 35.5°$, 38.7° and 38.9°, is also observed in all precursor powders. It is obvious that the spray pyrolysis powder contains the smallest amount of $\text{CuO}$, showing much weaker peaks than the others. This is consistent with our SEM/EDAX observation where $\text{CuO}$ grains were found much less often in the spray pyrolysis powder than in the others. The phase composition in the spray pyrolysis powder seems to be quite different from the others. With
SEM/EDAX, we also found grains of \((\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}\) (the 14–24 phase) in all powders. The 14–24 phase cannot be identified easily from the XRD pattern because its diffraction peaks overlap with some peaks from other phases.

In Fig. 3 we show the XRD patterns of all powders after sintering at 842°C for 24 h. A significant amount of Bi-2223 has formed in the spray pyrolysis powder. This can be observed from the diffraction peak of (002) at \(2\theta = 4.8^\circ\). However, only a small amount of Bi-2223 formed in the coprecipitation powder and little in the citrate gel powder. The formation of Bi-2223 phase with increasing sintering hours can be observed by the XRD peak area ratio of Bi-2223 (115)/[Bi-2223 (115) + Bi2212 (113)], where Bi-2223 (115) denotes the diffraction peak of (115) for Bi-2223 and Bi-2212 (113) denotes the diffraction peak of (113) for Bi-2212. As seen in Fig. 4, the development of the Bi-2223 phase occurs much faster in the spray pyrolysis powder than in the others, forming at least twice as much Bi-2223 in the first 24 h than the coprecipitation powder. Faster Bi-2223 phase formation can offer cost benefits in the OPIT process by reducing the total processing time. The spray pyrolysis powder offers clear advantages here. It is also shown in Fig. 4 that the Bi-2223 phase produced in coprecipitation powder is still less than that in spray pyrolysis powder at 96 h, where Bi-2223 has fully developed in both powders. Although the formation of Bi-2223 in the citrate gel powder has not fully developed (the curve has not saturated) after 96 h of sintering, it is unlikely, with longer sintering hours, that it could produce as much Bi-2223 as the spray pyrolysis powder could. Among the three, the powder prepared by spray pyrolysis is not only the most reactive to form Bi-2223 but also produces the most Bi-2223 phase.
Fig. 3. The XRD pattern for powders sintered at 842°C for 24 h.

Fig. 4. The XRD peak area ratios of Bi-2223 (115)/[Bi-2223 (115) + Bi2212 (113)] for powders sintered at 842°C.
The compositions of Bi, Pb, Sr, Ca, and Cu in the precursor powders were determined by ICP analyses. As seen in Table 1, the spray pyrolysis and citrate gel powders are consistent with the nominal compositions, to within 6%. However, the coprecipitation powder displays large deviation from the nominal composition: it is very deficient in strontium (9% less) and calcium (14% less), and has excess copper (11% more) and lead (6% more). The larger deviation suggests that coprecipitation is not as good in controlling the chemical composition. This might be attributed to the different solubility of different ions during the coprecipitation process.

4. Conclusions

There are differences in the properties of the precursor powders prepared using different processes. Coprecipitation produces a powder with the composition largely deviates from the nominal one. The spray pyrolysis powder seems to be quite different from the others in terms of the phase composition and the Bi-2223 phase formation. The powder produced by spray pyrolysis is more reactive to form Bi-2223 than those produced by coprecipitation and citrate gel.

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References