Oxygen release process of BSCCO powder during heat treatment

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In this paper, we report a new method to investigate the oxygen release process during heat treatment of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (BSCCO) powder, based on oxygen partial pressure measurement (OPPM) using an oxygen analyzer. The influence on oxygen release process of various processing parameters has been studied. Experimental results show that OPPM is a suitable method for investigation of the oxygen release process during heat treatment of BSCCO powder. It is suggested that oxygen release is related to decomposition of the Ca_2PbO_4 phase. © *2004 Kluwer Academic Publishers*

1. Introduction

Numerous studies have emphasized the importance of optimization of the powder-in-tube (PIT) BSCCO tape processing parameters in order to maximize the superconducting properties, and especially the critical current density. The processing parameters of most interest include the sintering temperature, the heating and cooling rate, and the oxygen partial pressure during annealing. The influence of oxygen partial pressure on the formation of $Bi_2Sr_2Ca_2Cu_3O_y$ (Bi-2223) phase has been well investigated [1–4]. An optimized oxygen partial pressure decreases the Bi-2223 phase formation temperature, enhances the reaction rate and expands the BSCCO formation temperature range. It is well known that the oxygen content in BSCCO materials is changeable, which depends on the oxygen partial pressure and temperature used in heat treatment. The oxygen content influences significantly the superconducting properties, such as the critical temperature (T_c) and current carrying capability. Buckley *et al.* [5] have reported that BSCCO materials release oxygen during the heating ramp and take up oxygen again during the cooling ramp. Goldacker *et al.* [6] have investigated the oxygen exchange during phase formation in Bi-2223 tapes by using macro-thermogravimetrical methods.

In this paper, we report a new method (oxygen partial pressure measurement, OPPM) using an oxygen analyzer to continuously monitor the oxygen release process of BSCCO precursor powder during heat treatment.

2. Experimental

Commercial precursor powder (P1) with a nominal composition of $Bi_{1.80}Pb_{0.33}Sr_{1.87}Ca_2Cu_3O_y$ was used in this study. The full phase composition of the powder was $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212), Ca_2PbO_4, $(Sr,Ca)CuO_2$ and $(Sr,Ca)_{14}Cu_{24}O_{41}$.

As a control, the influence on oxygen partial pressure during heat treatment of a furnace containing an empty crucible was first investigated. Experimental results showed that the oxygen partial pressure remained constant (at 8.50% O_2) during the heat treatment. This result indicates that changes of oxygen partial pressure during heat treatment can be related to variations of the oxygen content in the BSCCO powder.

The precursor powder P1 was heat treated in an atmosphere of 8.50% O_2 at different heating ramp rates, using various gas flow rates in a controlled atmosphere furnace. The heating ramp rate was varied from 50 to 200°C/h, and the gas flow rate was varied between 50 and 150 cm^3/min. The oxygen partial pressure was monitored using a Servomex xentra 4100 model oxygen analyzer connected to the outlet of the furnace.

Powder P1 was also calcined at 820°C for 5 h in air, resulting in powder (P2) consisting mainly of Bi-2212, Ca_2PbO_4 and 14/24 phases. A comparative study between the OPPM method and TG measurements was performed on powder P2. TG measurements were conducted using a SETARAM TGA92 thermal analyzer in a flowing atmosphere (8.50% O_2).

The OPPM oxygen analysis is based on the paramagnetic measurement method [7]. The accuracy of the

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oxygen analyzer was better than 0.02% over the entire (0 to 100%) range of oxygen. The phase composition of each powder was analyzed by X-ray diffraction (XRD) analysis using Cu K_α radiation. The presence of the lead oxide compounds was determined from the (110) peak of Ca_2PbO_4 ($2\theta = 17.63°$) [4]. The Ca_2PbO_4 phase was quantified using the ratio of the intensity of the (110) peak of Ca_2PbO_4 phase to that of the (115) peak of the Bi-2212 phase.

3. Results and discussion

Fig. 1 shows the variation of oxygen partial pressure versus time for different amounts of powder P1. It can be seen that the change of oxygen partial pressure follows a similar tendency for the different samples. Even though the mass of samples are different, the oxygen partial pressure starts to increase at the same temperature (approximately 695°C). A peak appears when the temperature reaches the dwell set point of 830°C. Subsequently the oxygen partial pressure decreases during the dwelling stage. The oxygen partial pressure begins to decrease further during the initial part of the cooling stage following the 3 h dwell. With increasing sample mass, the intensity of the oxygen partial pressure peak increases rapidly. The changes of oxygen partial pressure indicate that an oxygen release process occurs during the heating ramp stage and dwelling stage, and that an oxygen absorption process appears in the cooling stage.

The volume of released oxygen can be calculated from the measured oxygen partial pressure profile by use of the following equation:

$$V_e = \int_{t_1}^{t_2} F(P(t) - P_0)\mathrm{d}t \qquad (1)$$

where V_e is the volume of released oxygen in cm^3, t_1 and t_2 are the oxygen release beginning and finishing times in minutes respectively, F is the gas flow rate in cm^3/min, $P(t)$ is the oxygen partial pressure as a function of time, and P_0 is the oxygen partial pressure measured before oxygen release. In order to guarantee the reproducibility of the experimental results, the volumes of released oxygen are averaged over three measurements taken using the same processing conditions, including the amount of powder, gas flow rate
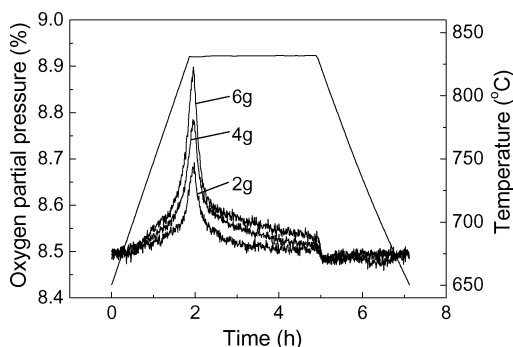
and heat treatment parameters. The relative error of the volume of released oxygen was less than ±5%. The volumes of released oxygen for samples of 2.00, 4.00 and 6.00 g were 7.6, 15.7 and 23.2 cm^3 respectively, which correspond to 3.8, 3.9 and 3.9 cm^3/g. This result shows that the volume of released oxygen per unit mass of sample is independent of sample mass.

Fig. 2 shows the variation of oxygen partial pressure versus time for powder P1 using different gas flow rates. It can be observed that the oxygen partial pressure starts to increase at approximately 695°C in each case despite the variations of gas flow rate. The volumes of oxygen released are 15.7, 15.5 and 15.4 cm^3 for samples heat treated with gas flow rates of 50, 100 and 150 cm^3/min respectively. This result indicates that the volume of released oxygen remains constant and is independent of gas flow rate when the amount of sample is fixed.

The variation of oxygen partial pressure versus time for powder P1 using different heating ramp rates is given in Fig. 3. It can be seen that the oxygen partial pressure starts to increase at approximately 695°C despite the variation of heating rate. The volume of released oxygen is 15.6, 15.7 and 15.2 cm^3 for samples heat treated with a heating rate of 50, 100 and 200°C/h respectively. This result indicates that the volume of released oxygen remains constant when the sample mass is fixed and is independent of heat ramp rate.

Fig. 4 shows the results of the comparative study between the OPPM method and TG measurements. Curve (a) is the weight loss curve for powder P2 in 8.50% O_2, curve (b) shows the relationship between oxygen partial pressure and time, and curve (c) shows the temperature profile of the heat treatment. It can be observed

Figure 2 Oxygen partial pressure versus time for powder P1 in 8.5% O_2 with different gas flow rates.

Figure 1 Oxygen partial pressure versus time for different amounts of powder P1 in 8.5% O_2 with a gas flow rate of 100 cm^3/min.
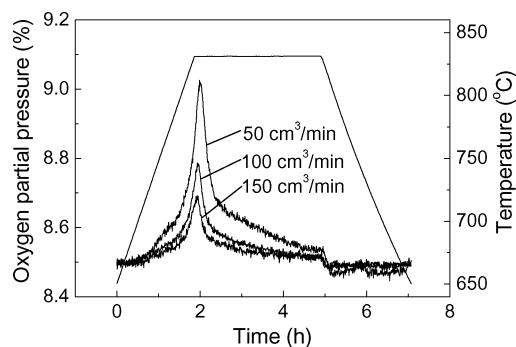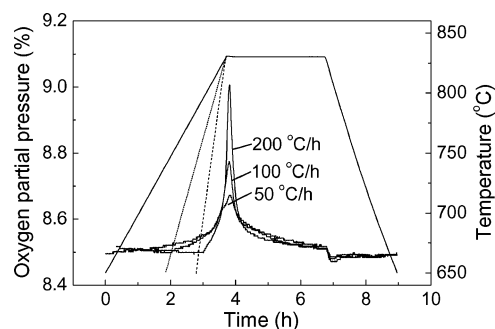
Figure 3 Oxygen partial pressure versus time for powder P1 in 8.5% O_2 with different heating ramp rates.
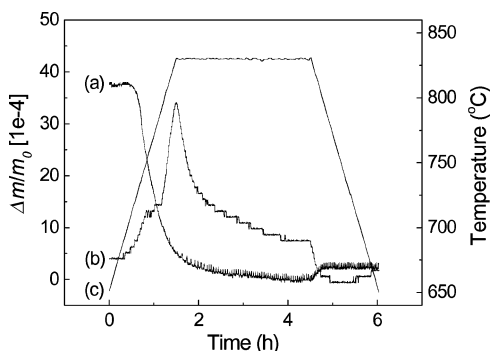
Figure 4 (a) TG curve obtained on powder P1 heat treated in 8.5% O_2, (b) oxygen partial pressure versus time for powder P1 in 8.5% O_2, and (c) the heat treatment profile.

that weight loss starts at approximately 700°C during the heating ramp, and that about 0.37% of the sample mass is lost during the combined heating ramp dwelling stages. After dwelling at 830°C for 3 h, the weight of the sample increases slightly during the cooling stage. The increase in mass is about 10% of the weight loss. The variation of mass of BSCCO powder during heat treatment could arise from two reasons. One reason is due to evaporation of volatile heavy elements, and the other reason is due to variations of oxygen content in BSCCO powder. It is known that in bismuth high-temperature superconductors Pb can be evaporated at high temperatures. However, Majewski *et al.* [8] have reported that Pb evaporation was not observed at temperatures below 870°C in the absence of Ag. It is believed therefore that Pb in BSCCO powders does not evaporate under the heat treatment conditions used in this study, and that the variation of sample mass is due to the variations of oxygen content in BSCCO powder. Consequently it is believed that oxygen release starts at approximately 700°C in the heating ramp, and that the amount of oxygen released during heating ramp and dwelling stage represents about 0.37% of the sample mass.

From curve (b) in Fig. 4, it can be seen that oxygen release starts at approximately 695°C. According to Equation 1, the volume of released oxygen for 4.00 g of powder P2 is 10.8 cm^3. The mass of released oxygen can be calculated to be about 15.4 mg, which corresponds to about 0.38% of the sample mass.

Results of the comparative study reveal that both methods suggest that oxygen release process starts at the similar temperature (at about 700°C). Moreover, the amounts of oxygen released obtained from the two methods are very close. It is known that the amount of oxygen released only depends on the mass of the sample, being independent of other heating process parameters, such as gas flow rate and heating ramp rate. So it is believed that the OPPM method is suitable to study oxygen release and absorption processes of BSCCO materials during heat treatment.

Fig. 5 shows the XRD results for the precursor powder P1, for samples quenched in air from different stages of the annealing treatment. The fractions of the Ca_2PbO_4 phase in the initial powder P1 and in the sample quenched from 690°C are 26 and 25% respectively. This result shows that the content of Ca_2PbO_4
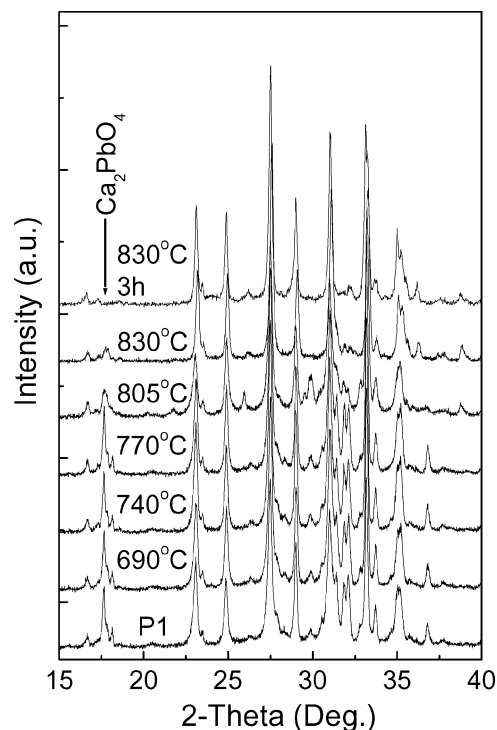

Figure 5 XRD results for (a) original powder P1, (b) samples quenched in air from different temperatures in the heating ramp stage, and (c) a sample quenched after dwelling for 3 h at 830°C.

phase remains constant before the oxygen release process. At the beginning stage of the oxygen release process (up to 805°C) the fraction of Ca_2PbO_4 phase decreases slowly with increasing temperature (22, 18 and 13% for samples quenched from 740, 770 and 805°C respectively). As the temperature rises to 830°C, the fraction of Ca_2PbO_4 phase is only 3%. After dwelling at 830°C for 3 h, the peaks of the Ca_2PbO_4 phase disappears.

The temperature at which the oxygen release begins is consistent with the decomposition temperature of the Ca_2PbO_4 phase. Furthermore, the trend in the change of oxygen partial pressure is similar to that for the decomposition of Ca_2PbO_4 phase. These similarities indicate that the oxygen release process of BSCCO powders during heat treatment could be related to decomposition of the Ca_2PbO_4 phase.

The (200)/(020) peaks of the Bi-2212 phase for the original powder P1 and for samples quenched in air from different stages of the annealing treatment are given in Fig. 6. It can be observed that the (200)/(020) peaks broaden gradually with increasing temperature, and a maximum value appears after dwelling for 3 h at 830°C. This indicates that the Bi-2212 phase transforms from a tetragonal phase into an orthorhombic phase gradually. Jeremie *et al.* [9] have reported that the tetragonal-orthorhombic transformation of the Bi-2212 phase is related to the incorporation of Pb into the Bi-2212 phase. The substitution of Pb for Bi in the Bi-2212 phase causes a change in the lattice parameters: the gradual addition of Pb leading to an increasing separation between the (200) peak and the (020) peak. The incorporation of Pb into the Bi-2212 phase is related to the Pb solubility in the (Bi,Pb)-2212 phase. The Pb solubility of the 2212 phase has been determined to be
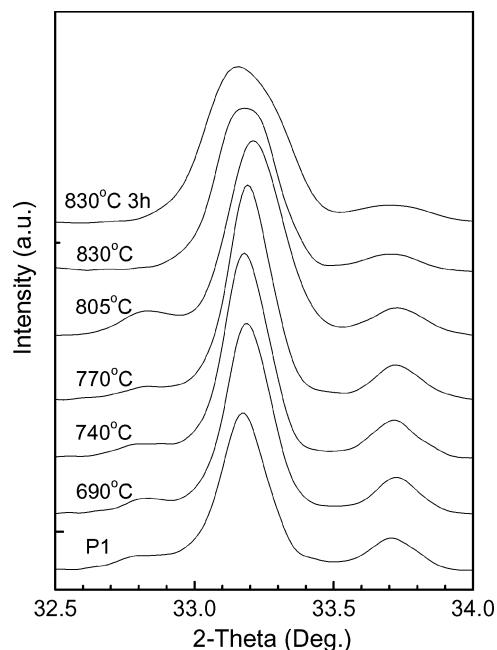
Figure 6 The (200)/(020) peaks of the Bi-2212 phase for (a) original powder P1, (b) samples quenched in air from different temperatures in the heating ramp stage, and (c) a sample quenched after dwelling for 3 h at 830°C.

a function of both the temperature and oxygen partial pressure [10, 11].

In the (Bi,Pb)-2212 phase lead has the oxidation state of Pb^{2+}, whereas in Ca_2PbO_4 it has the oxidation state of Pb^{4+}. When Ca_2PbO_4 phase decomposes and the oxidation state of lead is changed from Pb^{4+} to Pb^{2+}, oxygen must be released, and the mass of the sample will decrease at the same time. The results suggest that the oxygen release process occurring during the heating ramp and dwelling stage is related to decomposition of the Ca_2PbO_4 phase.

4. Summary

In this paper, we report a new method (OPPM) of using an oxygen analyzer to continuously monitor the oxygen partial pressure in order to investigate the oxygen release process of BSCCO powder during heat treatment. The experimental results show that OPPM is a suitable method to investigate oxygen release process of BSCCO powder during heat treatment. It is suggested that oxygen release process is related to the decomposition of the Ca_2PbO_4 phase.

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