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ARTICLE

Phase Evolution and Superconductivity of Bi-2212 Precursor Powder Prepared by Spray Pyrolysis

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Abstract: The $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) precursor powder was prepared by spray pyrolysis. The phase evolution during the heat treatment process and the superconductivity of wires were analyzed. Results show that the powder prepared by spray pyrolysis is spherical with the average particle size of 3.03 μm and the dispersion distribution. The phase evolution during the heat treatment process of powder includes four main reaction processes. The decomposition of nitrate and the pre-reaction process between components occur firstly at 527 °C. Then the $Bi_2Sr_2CuO_x$ (Bi-2201) phase is formed at 588 °C due to the high reactivity of spray powder. The Bi-2212 phase is generated at 780 °C, and the powder is completely melted at 834.2 °C. The heat treatment temperature window of the Bi-2212/Ag wire is very narrow. The critical current (I_c) is reduced by 31 A when the maximum heat treatment temperature (T_{max}) is changed by ±2 °C. When the optimal T_{max} of Bi-2212/Ag wire is 885 °C, the maximum I_c (4.2 K, 0 T) is 486 A. The critical current is increased to 712 A in the oxygen atmosphere during heat treatment.

Key words: Bi-2212; phase evolution; superconductivity

Due to the advantages of high upper critical field and easy processing into isotropic wires, $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) material is a very promising superconductor for high field applications, such as nuclear magnetic resonance, accelerator magnets, and nuclear fusion[1-4]. The multi-filamentary Bi-2212/Ag wire can be easily fabricated via the powder-in-tube (PIT) method. Besides, the kilometric Bi-2212/Ag wire has already been achieved[5]. The critical current (I_c) is continuously improved by the optimization of powder preparation, wire processing technique, and heat treatment process. The overpressure heat treatment (OP-HT) is a key breakthrough to fabricate Bi-2212/Ag wire with better filament density and grain connectivity[6]. The engineering critical current density (J_c) is increased by 8 times when the pressure is increased from 0.1 MPa to 10 MPa.

Generally, the precursor powder can significantly affect the I_c of Bi-2212/Ag wire. Therefore, various techniques have been developed to prepare Bi-2212 precursor powders, including the solid-state reaction[7,8], sol-gel method[9,10], co-precipitation method[11,12], and spray pyrolysis[13-15]. The properties of the Bi-2212 precursor powder are influenced by the phase composition, particle size, phase content, and powder homogeneity. The precursor powders of the kilometric Bi-2212/Ag wire are usually prepared by the spray pyrolysis and co-precipitation method. The precursor powder prepared by melt casting technique has the optimal J_c of 1014 A/mm^2 under the conditions of 4.2 K and 5 T[16]. The Bi-2212 precursor powders prepared by co-precipitation has the maximum J_c of 1456 A/mm^2 under the conditions of 4.2 K and 5 T[17]. The properties of Bi-2212 precursor powder can be further improved by the nanospray method: the J_c reaches 1810 A/mm^2 under the conditions of 4.2 K and 5 T[15,17]. Therefore, the spray pyrolysis exhibits good industrial application prospect.

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The critical current of the Bi-2212/Ag wire is greatly improved by the precursor powder prepared by spray pyrolysis technique. However, the characteristics and the phase evolution of the powders prepared by spray pyrolysis during the heat treatment process are rarely reported. In this research, the characteristics, phase evolution, and superconductivity of the Bi-2212 precursor powder prepared by the ultrasonic spray pyrolysis technique were investigated.

1 Experiment

The raw material $Bi_{2.17}Sr_{1.94}Ca_{0.89}Cu_2O_x$ [18] was the mixture of four nitrates. All nitrates were prepared as solutions with the ionic content of 1 mol/L. The precursor powder was prepared by the ultrasonic spray pyrolysis at the decomposition temperature of 800 °C. Then the powders were calcined in N_2-0.1vol% O_2 atmosphere at different temperatures to study the characteristics and phase evolution of the Bi-2212 precursor powders. The Bi-2212/Ag wire with 666 filaments (37×18 configuration) was fabricated by PIT technique, and the heat treatment was conducted by the partial melt process (PMP) at 0.1 MPa[16,17].

The melting behavior and phase evolution were analyzed based on the thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The phase composition was determined by X-ray diffraction (XRD). The powder morphologies were observed by scanning electron microscope (SEM). The critical currents of the Bi-2212/Ag wires were measured by the standard four-point probe with a criterion of 1 μV/cm.

2 Results and Discussion

During the ultrasonic spray pyrolysis, the nitrate solution is ultrasonically atomized into the micron-sized droplets which pass rapidly through the high temperature zone and are dehydrated to form the powder particles in the flowing gas. The decomposition and reactions occur in this process. Fig. 1 shows the particle size distribution and morphology of the as-prepared powders. The powders have the average particle size of only 3.03 μm, and the concentrated particle size distribution can also be observed. The powders are spherical with mutual diffusion distribution and no agglomeration can be observed. The reaction mainly occurs inside the particles, resulting in the uniformity of elements and phases.

Fig.2 shows TGA and DSC curves of the precursor powders in N_2-0.1vol% O_2 atmosphere at the heating rate of 10 °C/min. Three significant endothermic peaks at 527.0, 587.9, and 834.2 °C can be observed. The mass loss is 21.1% when temperature is increased from 400 °C to 600 °C. The Bi-2212 phase is generally formed above 700 °C. Therefore, the main reactions at 400~600 °C are the decomposition of nitrates and the reaction between the components.

The mass barely decreases above 600 °C. However, at the endothermic peak of 834.2 °C, a significant mass loss of about 1% is observed, which indicates the melting of Bi-2212 phase. Thus, the formation of Bi-2212 phase occurs at 587.9~834.2 °C.

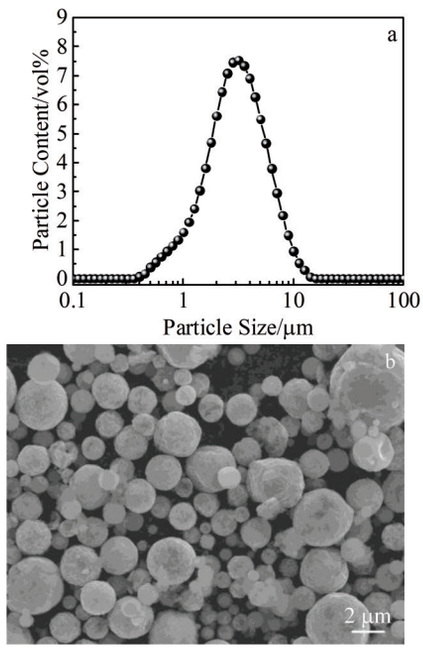

Fig.1 Particle size distribution (a) and morphology (b) of precursor powder prepared by ultrasonic spay pyrolysis

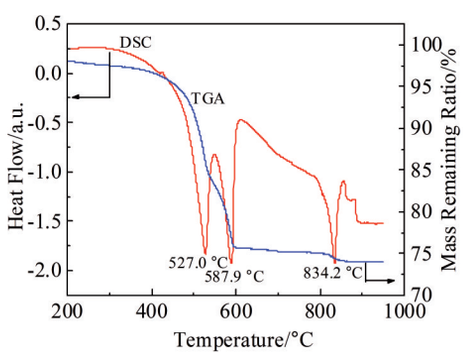

Fig.2 TGA and DSC curves of precursor powders in N_2-0.1vol% O_2 atmosphere at the heating rate of 10 °C/min

The heat treatments were conducted in the N_2-0.1vol% O_2 atmosphere at 527, 588, 780, and 834 °C for 12 h for phase evolution analysis of the precursor powders. SEM morphologies of the powders after heat treatments are shown in Fig.3. The powders after heat treatments at 527 and 588 °C maintain the spherical morphology, but their surface is coarser than that before heat treatment due to the decomposition of nitrates. The morphology changes when the heat treatment temperature is increased to 780 °C, as shown in Fig. 3c. The powders consist of flaky grains, which correspond to the $Bi_2Sr_2CuO_x$ (Bi-2201) or Bi-2212 phases. The average particle size of the powder is less than 1 μm. When the temperature is further increased to 834 °C, the powder melts completely, as shown in Fig.3d.

Fig. 4 shows the XRD patterns of the precursor powders

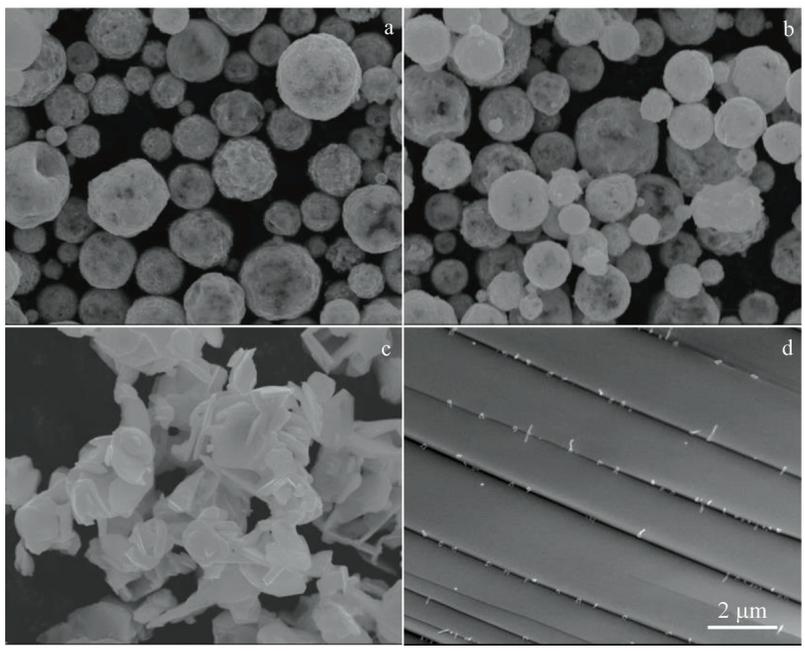

Fig.3 SEM morphologies of precursor powders after heat treatment at different temperatures for 12 h: (a) 527 °C, (b) 588 °C, (c) 780 °C, and (d) 834 °C

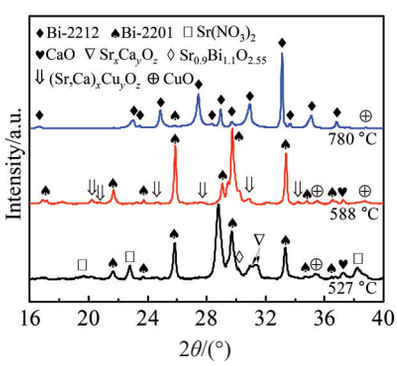

Fig.4 XRD patterns of precursor powders after heat treatments at 527, 588, and 780 °C for 12 h

after heat treatments at 527, 588, and 780 °C for 12 h in N_2-0.1vol% O_2 atmosphere. The precursor powder after heat treatment at 527 °C consists of nitrates and several oxides, including $Sr(NO_3)_2$, Bi-2201, CaO, CuO, Sr-Bi-oxide, and Sr-Ca-oxide. The Bi-2201 formation occurs at 588 °C due to the high reactivity of powders. When the temperature is further increased to 780 °C, the main phase of the precursor powder is completely transformed into the Bi-2212 phase, accompanied by a small amount of Bi-2201 phase and CuO. Therefore, the phase evolution can be divided into four stages. Stage I: $Sr(NO_3)_2$+Bi-2201+CaO+$Sr_{0.9}Bi_{1.1}O_{2.55}$+$Sr_xCa_yO_z$+CuO; Stage II : Bi-2201 + $(Sr, Ca)_xCu_yO_z$+CaO+CuO; Stage III : Bi2212+Bi-2201+CuO; Stage IV: complete melting reaction.

The Bi-2212/Ag wires were fabricated by the precursor powder after heat treatment at 780 °C for 12 h in N_2-0.1vol% O_2 atmosphere. The heat treatment process of the Bi-2212/Ag wire is according to the process in Ref. [17]. The short wires with the diameter of 1 mm suffered heat treatments with different maximum heat treatment temperatures (T_{max}). Fig. 5 shows the relationship between I_c (4.2 K, 0 T) and T_{max} of the Bi-2212/Ag wire. The peak I_c of 486 A is achieved at T_{max} of 885 °C, and the maximum I_c decrement is 31 A when the T_{max} changes by ±2 °C. It can be seen that the heat treatment temperature window of Bi-2212/Ag wire is very narrow.

The properties of the precursor powders are greatly influenced by the heat treatment temperature of Bi-2212/Ag wire. The optimal T_{max} is about 890.5 °C in Ref. [19], and the peak J_c appears at about 894 °C in Ref. [20]. However, the optimal T_{max} in this research is only 885 °C, indicating the significantly high reactivity of spray pyrolysis powders.

The Bi-2212 phase partially melts at T_{max} and nucleates through the slow cooling process to obtain the high-texture grains, thereby increasing the I_c of Bi-2212/Ag wires. Due to the low density of the wire and the carbon residue in the precursor powder, the voids are formed during the partial

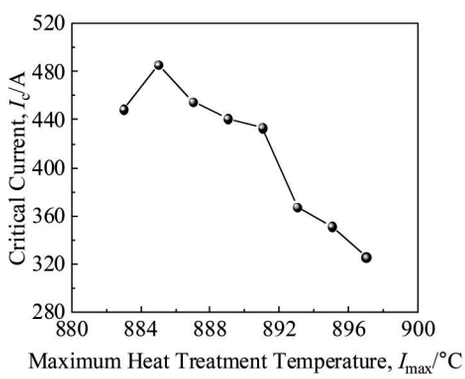

Fig.5 Relationship between I_c (4.2 K, 0 T) and T_{max} of Bi-2212/Ag wire

melting process. The relative content of the void is defined as the ratio of the void area to the whole wire area.

Fig.6 shows the relationship between the relative content of the void and T_{max}. The content of the liquid phase is increased gradually with increasing the T_{max}. These liquid phases gather together through the cracks between grains and finally form the voids during the cooling process. Therefore, the relative content of the void is monotonically increased with increasing the T_{max}. Because the maximum I_c occurs at T_{max} of 885 °C (Fig. 5), the optimal liquid phase content can be correspondingly obtained. The liquid phase content is continuously increased when T_{max} is higher than 885 °C, resulting in the excess formation of voids, which seriously blocks the current path. The liquid phase content is decreased when the temperature is lower than 885 °C, resulting in the poor grain texture, which is not conducive to the I_c enhancement of the Bi-2212/Ag wire.

Fig.7 shows the optical microscope (OM) images of the Bi-2212/Ag wires after heat treatment at different T_{max}. The void area is increased obviously with increasing the T_{max}. The voids appear firstly in the inner filaments and gradually in the outer filaments with increasing the T_{max}. The Bi-2212/Ag wire was

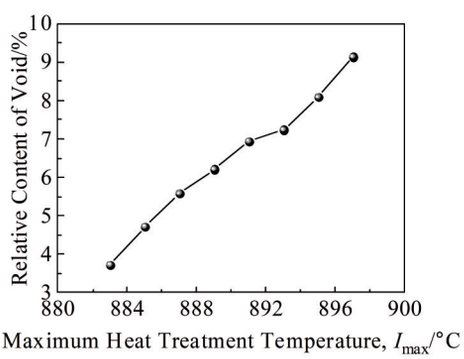

Fig.6 Relationship between relative content of void and T_{max} of Bi-2212/Ag wire

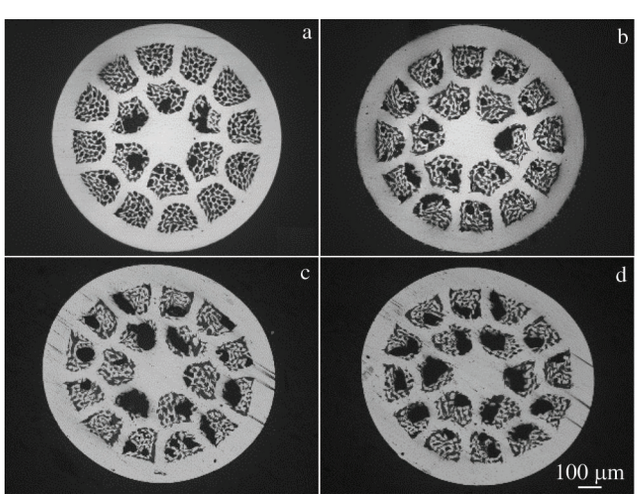

Fig.7 OM images of Bi-2212/Ag wires after heat treatments at different T_{max}: (a) 883 °C, (b) 887 °C, (c) 891 °C, and (d) 895 °C

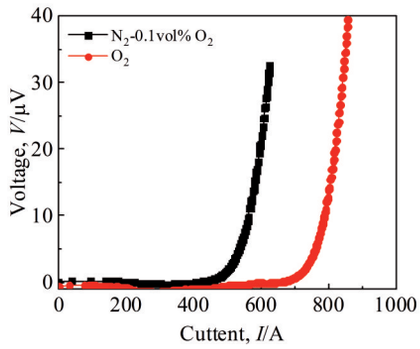

Fig.8 *V-I* curves of Bi-2212/Ag wires prepared by precursor powders after heat treatment at 770 °C for 12 h in N_2-0.1vol% O_2 atmosphere and at 860 °C for 12 h in O_2 atmosphere

heat-treated at T_{max} for only 0.2 h and then cooled slowly at the cooling rate of 10 °C/h. Due to the heat conduction, the cooling rate in the central area is slower than that in the outer layer of the wires. Thus, the central area contains more liquid phase, which leads to the difference of void area in the inner and outer filaments.

The Bi-2212/Ag wires fabricated by the precursor powders after heat treatments at 770 °C for 12 h in N_2-0.1vol% O_2 atmosphere and at 860 °C for 12 h in O_2 atmosphere were then heat-treated by PMP with the optimal T_{max} of 885 °C. Fig. 8 shows the voltage-current (*V-I*) curves of the two Bi-2212/Ag wires. I_c (4.2 K, 0 T) of the Bi-2212/Ag wire prepared by the precursor powder after heat treatment at 770 °C for 12 h in N_2-0.1vol% O_2 atmosphere is about 486 A, and the corresponding J_c is 619 A/mm^2. However, when the heat treatment atmosphere changes to oxygen, I_c is about 712 A, and the corresponding J_c is 907 A/mm^2, which is comparable to the J_c (4.2 K, 5 T) of 1100 A/mm^2 in Ref.[21]. The oxygen content in the heat treatment atmosphere of the precursor powder preparation has an important influence on the superconductivity of the Bi-2212/Ag wire.

3 Conclusions

1) The spray pyrolysis powders exhibit a concentrated particle size distribution and their average particle size is 3.03 μm. The powders are spherical and diffusively distributed without agglomeration.

2) The phase evolution of the spray pyrolysis powder consists of four stages, and the powder morphology changes. The Bi-2212 phase is formed during the heat treatment at 780 °C for 12 h in N_2-0.1vol% O_2 atmosphere.

3) The heat treatment temperature window of Bi-2212/Ag wire is very narrow. The maximum critical current (I_c) decrement is 31 A with the variation of ±2 °C in maximum heat treatment temperature (T_{max}). The optimal T_{max} is 885 °C, and the maximum I_c (4.2 K, 0 T) is about 486 A.

4) The oxygen content in the heat treatment atmosphere of the precursor powder has an important influence on the superconductivity of the Bi-2212/Ag wire. I_c (4.2 K, 0 T) of Bi-2212/Ag wire is increased to 712 A when oxygen is used as

the heat treatment atmosphere.

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喷雾热分解制备 Bi-2212 前驱粉末的相演变和超导性能

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摘　要：采用喷雾热分解技术制备高温超导$Bi_2Sr_2CaCu_2O_x$（Bi-2212）前驱粉末，并研究了粉末热处理过程中的相演变过程及线材的超导性能。结果表明，喷雾热分解制备的粉末平均粒度为3.03 μm，颗粒为球状并呈弥散分布。粉末在热处理过程中的相演变包含4个过程：粉末在527 ℃下主要进行硝酸盐的分解和组元之间的初步反应；由于喷雾粉末具有很高的活性，在588 ℃时生成$Bi_2Sr_2CuO_x$（Bi-2201）相；喷雾粉末在780 ℃发生Bi-2212相的成相反应；在834 ℃时粉末完全融化。Bi-2212/Ag超导线材的热处理温度窗口很窄，最高热处理温度T_{max}变化±2 ℃时，临界电流I_c的降幅达到了31 A。Bi-2212/Ag超导线材的最佳T_{max}为885 ℃，在该温度条件下制得的线材临界电流I_c（4.2 K，0 T）达到最高值，约为486 A。前驱粉末的热处理气氛为氧气时，线材的临界电流可以进一步提高到712 A。

关键词：Bi-2212；相演变；超导性能

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