Effect of grinding method on the precursor powder of Bi2223 and properties of strip

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Abstract. In this paper, the two kinds of precursor powders of BiPb2212 and CaCuO2 were prepared by double powder method and an improved coprecipitation method, and then the BiPb2212 powders were fabricated by mechanical grinding and hand grinding. The BiPb2212 powders and CaCuO2 powders were prepared by two kinds of grinding methods mixed with a certain proportion of grinding, the Bi2223 superconducting tape with 37 filaments were prepared by removing the carbon, filling tube and annealing. The XRD analysis, laser particle size analysis and the tap density test of the precursor BiPb2212 powders were carried out respectively by mechanical grinding and hand-grinding. The results showed that the phase composition, microstructure, particle size distribution and tube density detection were all significant differences by using two kinds of grinding methods. Finally, the superconductivity test of the treated strip results show that the critical current from the field for the Bi2223 multi-core strip at 77K is improved from 86A (hand-grinding method) to 127A (mechanical grinding method). Therefore, the Bi2223 precursor powder by using mechanical grinding method is more conducive to obtain high-performance.

1. Introduction

Bi2-xPb,xSr2Ca2Cu3Oy (Bi2223) superconducting tapes is one of the high-temperature superconducting materials. Powder-in-tube (PIT) is the mainstream technology for preparing Bi2223 superconducting tapes. High-quality precursor powder is the basis for the preparation of high-performance Bi-2223 tapes, the main characteristics of the parameters including the atomic ratio of the elements, phase composition and content, distribution of elements, particle size and distribution and carbon content and so on. When the atomic ratio is close, the phase composition, content, particle size distribution and elemental distribution of precursor powder have a great influence on the superconductivity of Bi2223 tape.

At present, the preparation methods of precursor powder include five kinds of solid phase mixing methods, such as sol-gel method [3], spray-drying method [4], chemical coprecipitation method [5] and spray pyrolysis method [6]. The main disadvantage of solid-phase mixing is that it is difficult to achieve uniform mixing, the sol-gel preparation method is complicated and difficult to control, and the spray drying method has the advantages of simple equipment, high preparation efficiency and easy introduction of impurities. For ordinary coprecipitation method, due to the difference in solubility of various substances, resulting in a larger deviation of the atomic ratio of the final powder, spray
pyrolysis method requires more expensive equipment support, and the current use of spray pyrolysis equipment made in China have not yet prepared high quality superconducting precursor powder.

Ordinary coprecipitation method by using water as a solvent, due to the solubility of metal oxalate in water is relatively large, it is likely to loss, and the solubility of each element is vary greatly, resulting in the final powder with atomic order. The ratio of deviations is larger, reducing the ultimate current capacity of superconducting tape. Improved coprecipitation method by choosing ethanol as solvent, and by strictly controlling the ratio of ethanol and water in the precipitation system, so the solubility of metal oxalate can be greatly reduced, and the precursor powder with similar design ratio can be obtained, while the ethanol can increase the filtration rate of coprecipitated slurry and shorten the drying time.

Bi2223 precursor powder can be synthesized in one step, which is called single powder process and is currently used by most research institutes. BiPb2212 and CaCuO2 powder (composed of Ca2CuO3 and CuO) can be synthesized first, and then the two powders can be mixed and ground, known as the dual-powder process [7,8]. Based on the improved coprecipitation method, Bi2223 precursor powder was prepared by dual powder process route. BiPb2212 was pulverized by different grinding methods. The effects of different grinding methods on phase composition (XRD analysis), Microstructure (SEM observation), particle size distribution and density of tube, and the final Bi2223 phase velocity and current carrying capacity were tested.

2. Experiments

The following are BiPb2212 and CaCuO2 powder preparation process.

First, weigh a certain amount of oxalic acid dissolved in ethanol to prepare a precipitant solution, and then follow the Bi1.8Pb0.34Sr1.9Ca1.0Cu2Ox ratio of Bi2O3, CuO, CaCO3, SrCO3 and Pb(NO3)2 dissolved in concentrated nitric acid, and configured as a nitrate solution.

The coprecipitation process shown in Fig.1, the nitrate solution was added to the precipitant solution at a certain speed by stirring, while we use the ammonia to adjust the pH of the precipitation system, and control the pH value in the range of 1.5 ± 0.05 [9]. Standing after precipitation filtration and drying, then the preparation of the pre-decomposition of the powder and the phase heat treatment, after each heat treatment, grinding the powder by using mechanical grinding and manual grinding methods.

CaCuO2 powder preparation process:

First, weigh a certain amount of oxalic acid dissolved in ethanol to prepare a precipitant solution, followed by Ca1.0Cu1.0Ox ratio of Cu, CaCO3 dissolved in concentrated nitric acid, configured as a nitrate solution, the same coprecipitation as shown in Fig.1, the nitrate solution was added to the precipitant solution during stirring, while we use the aqueous ammonia to adjust the pH of the precipitation system within a suitable range, standing precipitation and filter drying preparation of the powder pre-decomposition and heat treatment, after each heat treatment, grinding the powder by manual grinding.

![Fig.1. The draft of the improved co-precipitation process](image-url)
The BiPb2212 and CaCuO$_2$ powders were prepared by using two grinding methods with mixed and ground, according to the ratio of one to one substance, and the mixed grinding powder carbonized at high temperature, followed by manual packing, single-core wire processing, multi-core wire composite and processing, finally, prepared Bi2223 multi-core tape. The strip annealed twice in succession and annealed once for phase to obtain a Bi2223 multi-core tape with superconducting current-carrying capability.

The powders obtained by the two grinding methods were respectively subjected to the XRD analysis, the SEM observation, the laser particle size analysis and the tube tap density test. The final heat-treated strip was tested at 77 K using the standard four-lead method. The critical current is 1μV/cm.

3. Results and discussion

3.1 XRD analysis

BiPb2212 powder was prepared by the improved coprecipitation method after pre-decomposition and multiple sintering phase, after each heat treatment, we used manual grinding and mechanical grinding, it is found that the way can affect the final powder morphology, as shown in Fig.2, the main phase of the final powder is Bi2212 phase, but there is a difference in the second phase. In addition to the 1:1AEC phase, the Bi2201 phase exists in the hand-ground powder. We known the content and type of the second phase will affect the phase transformation process of Bi2223 in the subsequent strip and the superconducting current carrying capacity.

![Fig.2](image)

**Fig.2.** XRD patterns of BiPb2212 powders grinded by handwork and machine

3.2 SEM analysis

SEM photographs of powders prepared by different grinding methods are shown in Fig.3, the 1 and 2 are low magnification and high magnification of hand-milled powders, 3 and 4 are low and high-magnification pictures of mechanically milled powders. It is can be seen that the degree of dispersion of manual grinding powder is relatively low, the particles are larger, and there is obvious agglomeration, however, the mechanical grinding powder has a higher degree of dispersion, smaller particles and lower degree of agglomeration. The size of the powder particles by manual grinding in the high power electron microscope photograph is larger than 10 μm, and the particle boundaries are clear and clean, however, the powder particles by mechanical grinding are small, the size of the particle is less than 10 μm, the particle boundaries are fuzzy, not clean. The above comparison shows that the powder by using mechanical grinding played a better dispersion and broken due to high energy, stable output, and the output is unstable, and the grinding energy is low by manual grinding due to the existence of human factors, resulting in the degree of dispersion of the powder poor, the powder has not been well refined. Phase composition analysis and microscopic observation results show that mechanical grinding may be more conducive to obtain stable performance of multi-core superconducting tape.
Fig. 3. SEM photos of the BiPb2212 powders ground by handwork and machine

3.3 Performance analysis
The results of the laser particle size testing and analysis of powders prepared by different grinding methods are shown in Fig. 4a and Fig. 4b. It is found that the particle size of the hand-ground powder is larger than that of the mechanical grinding powder and the distribution of particle size is wide. The average particle size of the hand-ground powder is 16 μm, the distribution range is from 5 μm to nearly 79 μm, compared with the mechanical grinding powder, average size of particle is 5 μm, the distribution range is from 2 μm to 14 μm, which is consistent with the SEM analysis. Using the mechanical grinding, the precursor powder with small particle size and narrow distribution can be obtained, it is important that the fine particle size can improve the uniformity of the powder. At the same time, the Bi2223 phase can be accelerated and shorten heat treatment time, reduce manufacturing costs due to the higher activity of the fine particles.

Fig. 4. The granularity and distribution of the BiPb2212 powders (a) Grinded by handwork, (b) Grinded by machine
Fig. 5. The powder density of the tube (a) by machine-grinding powder, (b) by hand-grinding powder

The BiPb2212 powder prepared by different grinding methods was mixed and ground in proportion with the CaCuO₂ powder to obtain the packed precursor powder. The two powders were vibrated and packed, and the tap density was calculated and carried out in three groups respectively. The results are shown in Fig. 5a and Fig. 5b. It has been found that the precursor powder with the hand-ground has a lower tap density and a poorer stability between batches, with a large fluctuation of about 20 to 30%. While the precursor powder with mechanically ground has a high tap density, high stability between batches, the fluctuations is less than 5%. The comparison results show that the mechanical grinding powder is more stable than manual grinding powder with little difference between sample batches, which is more favorable for the preparation of the strip.

Fig. 6. The $U$-$I$ curves of Bi2223 tapes (a) after HT1 treatment, (b) final heat-treatment

Fig. 6a and Fig. 6b show the multi-core HT1 and the final UI curve after heat treatment with different grinding methods. Because of the heat treatment time of HT1 is longer, the difference between the powders is not shown. The test results of the current carrying capacity of the material showed that the $I_c$ (critical current) of the strip prepared by manual grinding powder was 86A, and the $I_c$ of the strip produced by the mechanical grinding powder was 127A. The $I_c$ increased greatly compared with the hand-ground powder. The results also well validated the above stages to conclude that both the mechanical properties of the powders prepared in the mechanical grinding mode have the same phase composition, particle size distribution and reactivity, the stability between batches is more
superior, and the prepared strip has higher current carrying capacity, it is more conducive to the practical development of Bi2223 superconducting tape.

4. Conclusion

In this paper, the dual-powder process was chosen to prepare the BiPb2212 and CaCuO2 powders using the improved coprecipitation method respectively. The results showed that the two kinds of grinding methods had no significant effect on the final second phase type and content, however, the mechanical grinding method is more conducive to obtain a high degree of dispersion, small particles, and narrow particle size distribution of the powder. However, the tap density of the powder prepared by mechanical grinding is larger, and the variation of packing density is smaller between different batches. The precursor powder prepared by two kinds of grinding methods, the critical current ($I_c$) test of HT1 and the final heat treatment of the two strips results show that the mechanical grinding powder was used to prepare the strip. The $I_c$ reached 127A at 77K, but the $I_c$ of the strip was only 86A by hand grinding the powder. Therefore, the mechanical grinding is more conducive to high performance Bi2223 multi-core strip.

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