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ARTICLE

Preparation of Boron Oxide Doped YBCO Superconducting Films by One-step Heat Treatment

Li Yingnan, Ning Zixu, Mi Zhaoyin, Wu Jinqiu, Qi Xiaotong

Institute of Resources and Environmental Engineering, School of Metallurgy, Northeastern University, Shenyang 110819, China

Abstract: In order to improve the efficiency of chemical preparation of $YBa_2Cu_3O_{7-\delta}$ (YBCO) with long taps, the pyrolysis of traditional process preparing precursor film needs to be reduced to one step, so the crystallization process should be directly connected to the former without the cooling of pyrolysis. Replacing copper trifluoroacetate with copper isooctanoate can alleviate the centralized heat release and the contraction of the precursor film during pyrolysis. In this study, a suitable amount of boric acid was added into the precursor solution with total cation concentration of 1.0 mol/L. After a continuous heat treatment YBCO superconducting film was obtained. Utilizing the flow state of boric acid at 200~500 °C, boron oxide was doped into YBCO film which becomes denser and smoother by filling some pores. Compared with that one prepared by undoped precursor solution under the same conditions, the former shows higher superconductivity.

Key words: YBCO; boric acid; boron oxide

The technique of metal organ deposition (MOD) used to prepare YBCO superconducting film has been developed for decades and widely applied in the preparation of electronic thin films for its potential large-scale production accessibility and low cost[1,2], but there are still problems to be solved in the field of continuous preparation of YBCO superconducting long strip by MOD method. For example, the preparation of the YBCO precursor film generally undergoes two passes of coating, pyrolysis, and furnace cooling to enter the final high-temperature crystallization to form YBCO superconducting film, which restricts the efficiency of producing YBCO superconducting film with a continuous MOD method. If a continuous uninterrupted heat treatment can be used and finally a certain thickness of YBCO superconducting film is obtained, then the experimental basis for the continuous production of YBCO strip by the MOD method can be provided, and the texture damage of metal substrate and buffer layer caused by high temperature can be reduced[3-5]. It has been previously reported[6] that PVB (polyvinyl butyral) was added to the precursor solution to prevent sharp shrinkage, reduce the pyrolysis process, and prepare a YBCO superconducting film by a one-step heat treatment at a certain concentration. In this study, a new additive (boric acid) was used, which showed a flowing state between 200 to 500 ºC[7], to fill some pores and smooth the shrinkage process of YBCO film, and the YBCO film was directly synthesized by one-step heat treatment. The YBCO film prepared by boric acid mixed in precursor solution was compared to that synthesized in the same conditions but using non doped precursors.

1 Experiment

In the experiment, it was weighed according to the ratio of $n(Y(CH_3COO)_3)$:$n(Ba(CH_3COO)_2)$:$n(Cu(CH_3COO)_2)$ as 1:2:3. In the process of formulating solution, the yttrium acetate and barium acetate were separately dissolved in an appropriate amount of deionized water, and after mixing for 2 h dripped trifluoroacetic acid with 10% excess, the mixture was poured into a distillation flask and distilled under the degree of vacuum –0.09 MPa until the gasification rate was up to 1/2. Then an appropriate amount of absolute ethanol was added to the distillation flask to continue the distillation under vacuum, and the distillation was repeated several times until the pH of the liquid in the distillation

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Corresponding author: Li Yingnan, Ph. D., Institute of Resources and Environmental Engineering, School of Metallurgy, Northeastern University, Shenyang 110819, P. R. China, Tel: 0086-24-83687719, E-mail: liyn@smm.neu.edu.cn

flask was close to 6.5. The copper isooctanoate solution previously dissolved in absolute ethanol was introduced into the distillation flask, and the volume was controlled by heating and stirring until the total cation concentration of the mixture reached 1.0 mol/L. The obtained precursor liquid was separated to two parts and marked as L1 and L2. Boric acid (purity: 99.9%) having a total cation amount of 5% was added to L2, and the mixture was stirred until the boric acid was dissolved completely and the obtained precursor liquid was a dark green viscous liquid. The coated film was accomplished by spinning on a single crystal $LaAlO_3$ (LAO) at 5000 r/min for 30 s. The wet film was dried at 80 °C for 30 min in an oven and then quickly placed into an 80 °C preheated tube furnace. The heat treatment process integrated 400 °C pyrolysis and 800 °C crystallization to one step. Fig.1 shows a temperature-time recording curve of the one-step heat treatment process.

The crystalline structure and surface morphology of YBCO films were characterized by means of X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force scanning electron microscope (AFM). The existence form of boron element was analyzed by X-ray photoelectron spectroscopy (XPS). The critical temperature T_c was examined by both the conventional DC four-probe method and magnetic induction method used an Signal Recovery® 7225 lock-in amplifier with the full scale as *y*-axis value when the output was set 0.9 V and 20 kHz and the sensitive was set 100 mV. The critical current J_c of YBCO film was measured by the conventional DC four-probe method at 77 K, in self-field.

2 Results and Discussion

2.1 Crystalline structure and surface morphology of the YBCO film

The boric acid added to the precursor liquid will finish decomposing in the pyrolysis process of YBCO precursor film, and the following chemical reactions occur:

$$H_3BO_3 \rightarrow H_2O + HBO_2 \quad (1)$$

$$HBO_2 \rightarrow H_2O + B_2O_3 \quad (2)$$

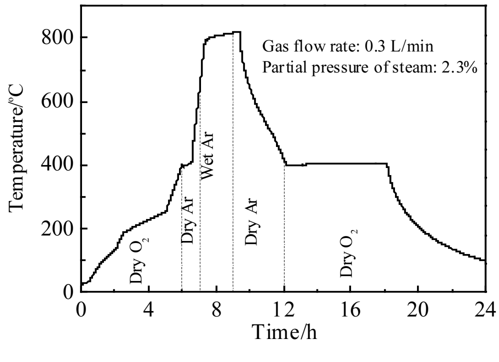

Fig.1 Temperature-time recording curve of the one-step heat treatment process

After boric acid is heated to 100 °C, due to the constant loss of moisture, it first becomes metaboric acid. There are three variants of metaboric acid with the melting points of 176, 201 and 236 °C, respectively. The dehydration of boric acid can be declared to end by forming metaboric acid. With heating continued the water will be removed to form boron oxide. Amorphous boron oxide has not fixed melting point and does not exhibit characteristic peaks in XRD patterns. It begins to soften at 325 °C and diffuses into the YBCO precursor film after all of it becomes liquid at 500 °C.

YBCO precursor film completes pyrolysis at 300~400 °C, which is the main period of defect formation[8], especially for thick film, that is easier to cause defects such as agglomeration, shrinkage and wrinkles[9]. Boron oxide can remain soft in this temperature zone and also maintain the initial dispersion state of metal oxides in precursor film, avoiding agglomeration, etc. In the subsequent rapid heating section up to 400 °C, boron oxide is gradually converted into liquid dispersed into the gap between YBCO phases so that the superconducting film will become denser, avoiding the occurrence of shrinkage cracks. This might have a positive effect on the resistance to temperature stress fatigue after YBCO multiple superconducting transitions[10].

X-ray diffraction patterns are shown in Fig.2. The intensity of YBCO (00*l*) diffraction peaks were very high and the two samples both formed *c*-axis grown YBCO grains obviously. Under the same XRD scanning conditions, the (00*l*) diffraction peaks of B doped YBCO film were stronger significantly indicating the degree of crystallization is higher or the *c*-axis oriented YBCO crystal in the XRD scanning area is much more, which should be confirmed by further criterion such as the gradient of *R*-*T* or *M*-*T* curve. Compared with the YBCO (00*l*) peak positions, it could be found that the (00*l*) peak position of the boron oxide doped YBCO increased by about 0.1°. According to the X-ray diffraction Bragg's law, the YBCO lattice length of *c*-axis could be shortened correspondingly, which could be caused by boron doped.

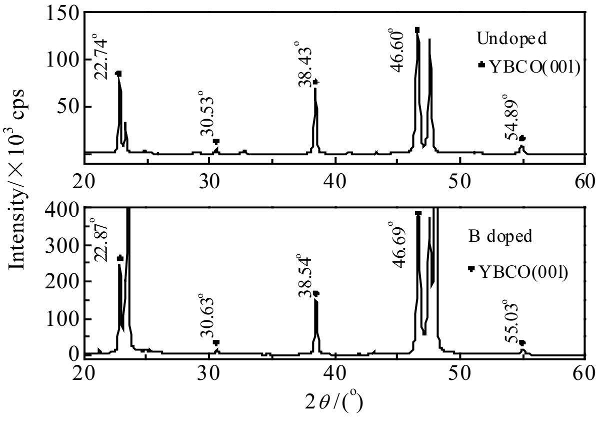

Fig.2 Typical XRD patterns of undoped and B doped YBCO film

There could be two main forms of boron doped. One is that the independent phase (boron oxide) has diffused among the YBCO grains, but it is not enough to cause the change of the YBCO lattice size. The other one, substitution of some atoms such as B atom into the interior of the YBCO lattice may be responsible for the change in the axial length of the *c*-axis lattice.

Compared with the results of SEM micrographs, there are obvious differences between the undoped and the B doped YBCO films, as shown in Fig.3.

Fig.3a is the SEM images of undoped YBCO superconducting film. The grains show obvious orthogonal arrangement with some grains like needle resulted from *a*-axis preferential orientation growth. The formation of pores might have two reasons, one is the HF, CO_2 and steam generated during the heat treatment; the other is that the growth rate of YBCO along the *a*-axis direction and the *c*-axis direction is not equal. The grains firstly propagate along the *a*-axis direction during the growth beginning, then merge and grow along the *c*-axis direction together due to the epitaxial effect which also causes the shrinkage in-plane and the airway through *c*-axis direction. Orthogonal crystal grains appeared in some local regions, and the acicular crystal grains could be YBCO with *a*-axis orientation (*c*-axis parallels to in-plane), which have an adverse effect on superconductivity in the entire YBCO film. The Cu-O planes of the *c*-axis grains communicate with each other to provide a flow channel for the superconducting electron, and there is also electron exchange between the different Cu-O faces, so the YBCO grains have conductive characteristics at normal temperature, and conventional electrons can flow in the *c*-axis direction. When YBCO enters the superconducting state, the *a*-axis grains block the continuation of the *c*-axis grain Cu-O plane, because only a large number of interconnected Cu-O planes in the long-range dimension could bear the relative larger superconducting current. Fig. 3b shows SEM micrograph of B doped YBCO superconducting film, the film surface is denser and smoother, and the porosity on the scanning area is more decreased and the volume of pores seems reduced than former, acicular crystal grains and the orthogonal arrangement form of YBCO nearly disappear. It might be due to boron element well-distributed in the YBCO film by the form of a certain compound.

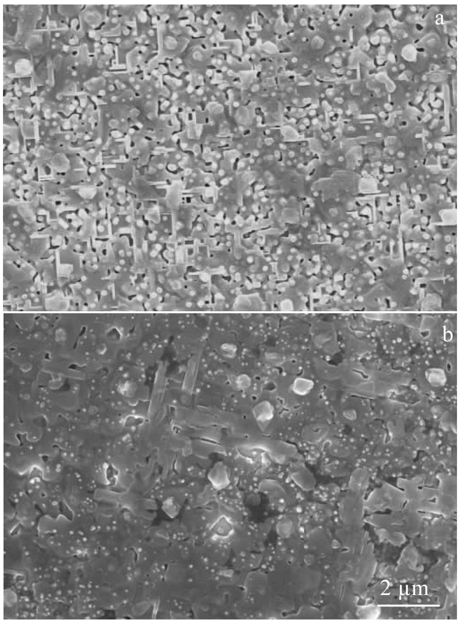

Fig.3 SEM images of undoped (a) and B doped YBCO film (b)

As shown in Fig.4, the film thickness of the two samples is 170 and 410 nm. The thickness of the B-doped YBCO film increases obviously because the addition of boric acid increases the viscosity of the precursor solution.

As shown in Fig. 5, the surface roughness was investigated by AFM, and an area of 5 μm×5 μm were typically obtained in a contact mode. The surface roughness of undoped and B doped YBCO film was 62.7 and 49.2 nm respectively. The former maintained a distinct orthogonal form obviously similar to Fig. 3a, and the other were denser and smoother as shown in Fig 3b.

2.2 Existence form of the boron element

For all XPS analysis, the C 1s (284.6 eV) from surface contamination is chosen to be a reference energy[11, 12].

As shown in Fig. 6, it is very obvious that the B 1s (B_2O_3) peak and the valence band peak (B_2O_3) appear at 192.29 eV and 190.03 eV respectively, but B 1s (B) peak is not found near to 188 eV. It can be confirmed that boric acid have decomposed to B_2O_3 and doped into the YBCO grain gap.

Since there are no obvious characteristic diffraction peaks of borate, boric acid and boron, or even boron oxide crystals in XRD pattern shown as Fig.2, boron element most likely exist in the form of boron oxide, considering amorphous boron oxide has no characteristic peak of XRD, which is consistent with the results of XRD pattern and XPS spectra.

2.3 Superconductivity of the YBCO film

Fig.7 displays the T_c (onset) of B doped YBCO supercon-

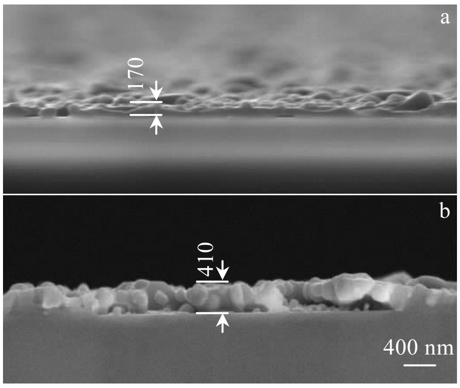

Fig.4 SEM images about cross section of undoped (a) and B doped YBCO film (b)

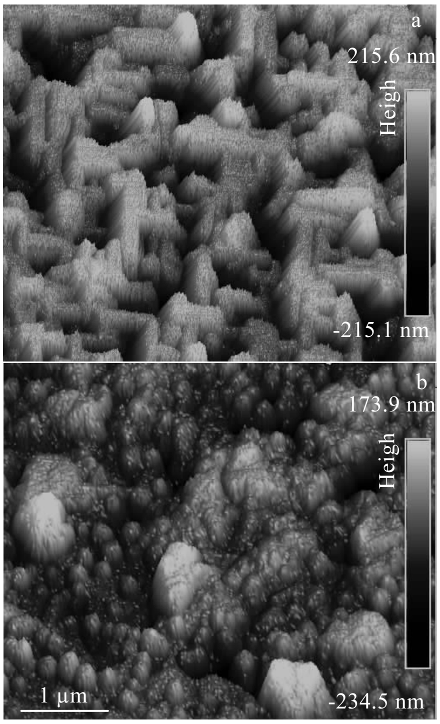

Fig.5 AFM images of undoped (a) and B doped YBCO film (b)

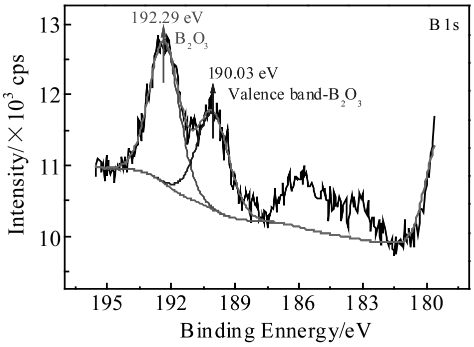

Fig.6 B 1s XPS spectra of B doped YBCO film

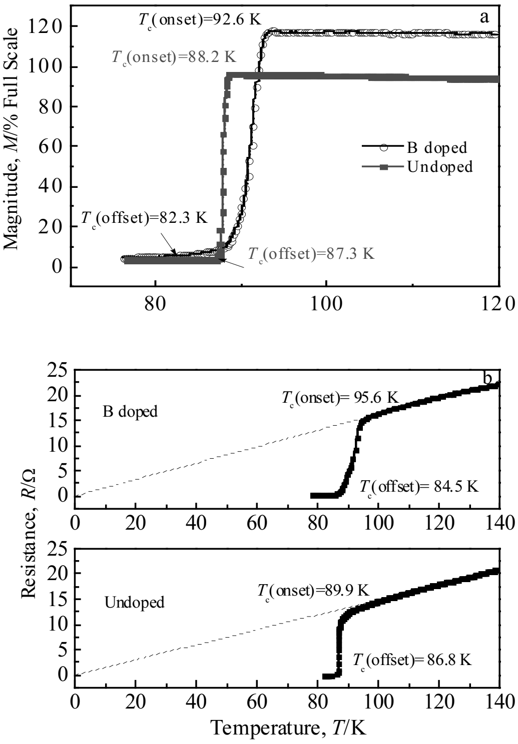

Fig.7 *M-T* (a) and *R-T* (b) curves about critical temperature T_c

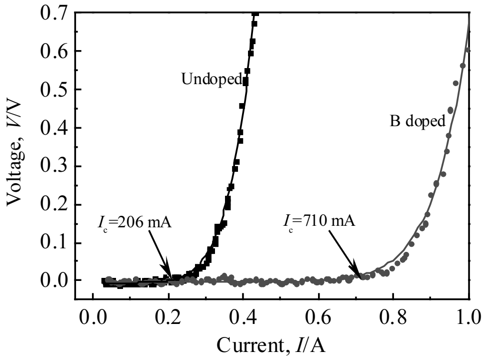

Fig.8 *V-I* curves about critical current I_c of YBCO film

ducting film is higher than that of undoped one, but the T_c (offset) is lower, measured no matter by the conventional DC four-probe method or magnetic induction method. The undoped YBCO superconducting film shows a sharper superconducting transition temperature than that one due to B doped leading to a slight degradation of YBCO crystallinity[13]. Review the XRD patterns shown as Fig. 2, the (00*l*) diffraction peaks of B doped YBCO film are stronger significantly not for the degree of crystallization is higher but the *c*-axis oriented YBCO crystal in the XRD scanning area is much more because of the thickness increasing shown as Fig.4 previously.

Fig.8 shows the transport voltage-current curve (*V-I* curve) of YBCO film. The YBCO films were patterned to be micro-bridge with width of 250 mm by etching, length of 4 mm and thickness of about 170 nm and 410 nm as shown in Fig.4. The critical current of the micro-bridge is 206 and 710 mA respectively of undoped and B doped YBCO film, which corresponds to the critical current density J_c of 0.48 and 0.69 MA/cm^2, respectively. B doped YBCO film shows a higher critical current density than the undoped one under the same preparing conditions, which may be attributed to its good in plane and out of plane texture, dense microstructure with good inter granular connectivity. Additionally, after the superconducting film is reciprocated many times between liquid nitrogen temperature zone and room temperature, some water will condense in the surface or infiltrate into the interior in the form of ice or water, which is unfavorable for the superconducting property of YBCO, then the B_2O_3 is blocked in the pores in a form of filler which impedes the penetration of water, and may be responsible for the better superconductivity of the B doped YBCO film.

3 Conclusions

1) YBCO superconducting film can be prepared by one-step continuous heat treatment.

2) B_2O_3 coming from the boric acid pyrolysis is filled in YBCO grains, as the form of B doped, which makes YBCO film thicker, denser and smoother.

3) The critical temperature T_c, the critical current I_c and the critical current density J_c of B doped YBCO superconducting film are higher than those of the undoped one under the same preparing conditions.

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一步热处理制备氧化硼掺杂的 YBCO 超导膜

李英楠，宁梓旭，米兆垠，吴金秋，齐晓童

(东北大学 冶金学院资源与环境工程研究所, 辽宁 沈阳 110819)

摘　要: 为了提高化学法制备长带YBCO的效率，传统的前驱膜多次热解过程需要被缩减为一次，热解后不经过降温直接连接YBCO的晶化过程。采用异辛酸铜替代三氟乙酸铜，可以缓解热解过程的集中放热，缓解前驱膜的收缩。适量硼酸被添加进 1.0 mol/L 的前驱液，经过一次连续热处理，YBCO 超导膜被制备出来。利用硼酸在 200 至 500 ℃的流动态这一特性，氧化硼填充进 YBCO 气孔，所得 YBCO 膜更加致密、光亮，与同样条件无掺杂前驱液制备的 YBCO 对比，具有更高的超导电性。

关键词: YBCO；硼酸；氧化硼

作者简介：李英楠，男，1977 年生，博士，东北大学冶金学院资源与环境工程研究所，辽宁 沈阳 110819，电话：024-83687719，E-mail: liyn@smm. neu.edu.cn