Intermediate Phase Evolution of YBCO Superconducting Films Fabricated by Fluorine Free MOD Method

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Abstract. The second generation high temperature superconducting tapes, which use ReBCO film as superconducting layer, are considered to have enormous potential in practical applications because of its high operation temperature (up to 77 K), high superconducting performance under strong field and good mechanical properties relative to other practical superconducting wires / tapes. Among its preparation processes, fluorine free-metal organic deposition (FF-MOD) technique has been a research hotspot in recent years because of its unneccessity of vacuum environment, fast pyrolysis and crystallization growth rate, and environmental friendliness. In this paper, YBCO films were prepared on the CeO₂ / IBAD-MgO / Y₂O₃ / Al₂O₃ / Hastelloy C276 technical substrate by FF-MOD technique. To systematically study the process of its phase evolution, the samples were quenched in different temperatures and followed by the characterization of XRD, ATR-IR and SEM. It is shown that the reaction between BaCO₃ and the oxides of Y and Cu elements does not produce YBCO directly, but experienced a more complicated intermediate process. Besides, the formed YBCO crystals are randomly oriented at first, and then converted into a biaxially textured structure.

1. Introduction
In recent years, superconducting technology has become a hot spot in many application scenario including power transmission cables, transformers, current limiters, magnetic levitation, magnetic resonance and particle accelerators. The second generation of high temperature superconducting (2G-HTS) tapes, which known as coated conductor, are considered to have a good prospect in practical applications. Because they have high critical temperature ($T_c$), high critical current density ($J_c$) and good mechanical properties (small critical bending radius[¹], high critical tensile strength[²]).

By now, the main technical issue of preparing high-performance ReBCO coated conductors is to deposit biaxially textured ReBCO films on biaxially textured substrates[³]. In this process, three methods were wildly used: pulsed laser deposition (PLD), metal organic chemical vapour deposition (MOCVD) and metal organic deposition (MOD). Among them, the MOD method does not require high vacuum environment (which means low equipment cost), and has the unique advantage of
making wide tapes \cite{4}. However, in the YBCO films made by MOD method in earlier years, the BaCO$_3$ generated in pyrolysis process was still stable at the temperature of YBCO formation, and remained on the grain boundary, which is the obstacle of current transmission in the superconducting state \cite{5}. Only by strict controlling of the temperature and oxygen partial pressure during heat treatment \cite{6}, YBCO films with $J_c > 1$ MA/cm$^2$ (77K, 0 T) could be prepared. On the other hand, Trifluoroacetic acid metal organic deposition (TFA-MOD) method was proposed by Gupta et al\cite{7}, which replaced the BaCO$_3$ intermediate phase by more stable BaF$_2$ during the pyrolysis process by introducing F element into the precursor solution, and eliminated F element in the form of HF gas in the crystallization process\cite{8}. After extensive development, YBCO films with $J_c$ of more than 5 MA/cm$^2$ and commercial long tapes with critical currents of more than 200 A (77 K, 0 T) could been prepared by the TFA-MOD method \cite{9} with wider process window.

However, in TFA-MOD method, the crystallization speed is severely limited by the removal speed of HF gas \cite{10}, and the HF gas itself is harmful on plants and animals. In contrast, the fluorine-free metal organic deposition (FF-MOD) method which has been studied before the invention of TFA-MOD method, is more environmentally friendly and more time efficient in heat treatment process. So in recent years, the FF-MOD technology has drawn the researchers’ attention again \cite{11}. As introduced above, during FF-MOD process, the Ba element exists in the form of BaCO$_3$ after the pyrolysis process. Therefore, a more in-depth study on the phase evolution of BaCO$_3$ and YBCO in the heat treatment process will be important for improving the performance of YBCO films made by FF-MOD method. Xu et al \cite{12} removed BaCO$_3$ phase by using trimethylacetate as a precursor and introducing a wet atmosphere in the crystallization process in which BaCO$_3$ reacts with H$_2$O to form Ba(OH)$_2$. Then Ba(OH)$_2$ react with other oxides to form YBCO phase. Vermeir et al. \cite{13} studied the phase evolution of YBCO films deposited on STO single crystal substrate by a water based FF-MOD solution. They found that BaCO$_3$ would experience a three-step reactions: first BaCO$_3$ reacts with CuO to form BaCuO$_2$ which will continue to react with CuO to form a liquid phase. At last, the liquid phase reacts with Y$_2$O$_3$ to form YBCO crystals.

In this paper, a solution based on yttrium acetate, barium acetate, copper acetate and propionic acid was used to prepare YBCO thin films on a technical substrate (CeO$_2$/IBAD-MgO/Y$_2$O$_3$/Al$_2$O$_3$/Hastelloy C276). The phase evolution of BaCO$_3$ and YBCO during the crystallization process is studied.

2. Experiments

2.1. Solution preparation and coating

A precursor solution \cite{14} with total cation concentration of 1.5mol/L was prepared by mixing Y (CH$_3$COO)$_3$·4H$_2$O, Ba (CH$_3$COO)$_2$, Cu (CH$_3$COO)$_2$·H$_2$O salts and propionic acid. The wet films were uniformly coated on CeO$_2$ / IBAD-MgO / Y$_2$O$_3$ / Al$_2$O$_3$ / Hastelloy C276 technical substrates by dip coating method with SYDC-200 pulling coating machine, the pulling speed was 1.5mm/s.

2.2. Heat treatment

![Figure 1. Diagram of temperature - atmosphere in heat treatment process](image-url)

[Figure 1. Diagram of temperature - atmosphere in heat treatment process]
The heat treatment process, as shown in Figure 1, is divided into three steps: pyrolysis, crystallization and oxygen annealing. During the pyrolysis process, the temperature was raised to 470 °C at a rate of 10 °C/min and held for 30 minutes within an atmosphere of pure wet O₂ flow (500ml/min). During the crystallization process, the temperature was raised to 800 °C at a rate of 20 °C/min and held for 30 minutes in an atmosphere of 100ppm O₂ flow (300ml/min, balanced with N₂), the atmosphere was kept until the end of the cooling. (To study the phase evolution, samples were quenched at different temperatures in the crystallization process.) The oxygen annealing of the crystallized YBCO films was conducted at 450 °C held for 180 minutes in an atmosphere of pure dry O₂ flow (50ml/min).

2.3. Characterization
The phase composition and texture of the samples were studied by a Bruker D8 Advance X-ray Diffraction (XRD) instrument using CuKα1 (Kβ signal included) signal source with a Bruker VÅNTEC-500 area detector. The surface micro-morphology of the samples were studied by Zeiss Auriga scanning electron microscope (SEM) in Inlens mode. Using a Nicolet Model 6700 Infrared Spectrometer, Fourier transform infrared (FT-IR) spectra of the sample were obtained under attenuated total reflection (ATR) mode. BaCO₃ residues up to 2% by mass can be detected by this method. The hysteresis loop of the fully processed films were obtained by a Physical Property Measurement System (PPMS). The critical current density (Jc) was calculated using equation (1), which is based on the extended Bean critical state model [15]:

\[
J_c = \frac{20 \Delta M}{\nu a \left(1 - \frac{a}{3b}\right)}
\]

Where \( \Delta m \) is the opening of the magnetization hysteresis loop; \( a, b \) are the length and width of the sample respectively (\( a \leq b \)); \( \nu \) is the volume of the YBCO film.

![Infrared Absorption Spectrum on samples quenched in different temperature on artificial substrate](image)

Figure 2. Infrared Absorption Spectrum on samples quenched in different temperature on artificial substrate
3. Results and Discussions
When samples were prepared on technical substrate, XRD and ATR-FT-IR characterization were performed on the samples quenched from different temperatures, the results is shown in Figure 2, Figure 3 and Figure 4. In order to give better expression to the change of BaCO$_3$ phase, larger scale is used in the $\chi$ direction in Figure 3 (a), 3 (b), and YBCO diffraction pattern is labeled with the abbreviation Y, and all patterns from the substrate(such CeO$_2$ at 32.7° and Y$_2$O$_3$ at 28.8°) were labeled with symbol “◊” in figure 3.

As can be seen from the figure: 1) In the infrared spectrum, all peaks other than BaCO$_3$ phase are derived from the substrate itself; 2) the BaCO$_3$ phase in the film is always exists until the temperature reaches 660 °C. When the temperature reaches 640 °C, there is still obvious BaCO$_3$ phase on the XRD and ATR-FT-IR characterization results. At this time, the surface is mostly uniformly distributed Nano grains; 3) When the temperature reached 660 °C, BaCO$_3$ phase was no longer visible in the XRD characterization, and YBCO(103) did not appear. In the infrared absorption spectrum, the corresponding absorption peak of BaCO$_3$ could still be observed, but with an obvious intensity attenuation, which demonstrated that BaCO$_3$ has been involved in the chemical reaction at this stage. No YBCO product was detected, and there was no significant change in the film surface morphology; 4) YBCO (103) began to appear when the temperature reached 680 °C. At this stage, the BaCO$_3$ phase in the infrared absorption spectrum completely disappeared and crystalline morphology (lamellar
grains) began to appear on the surface of the film; 5) With further increase of temperature, coexistence of YBCO (00l) and YBCO (103) begin to appear in XRD result, and as the temperature increases, the intensity of the YBCO (00l) peaks and number and scale of lamellar crystals are also increasing. 6) When the temperature reached 800, the (00l) spots of YBCO phase were bright and sharp without the coexistence of (103) ring. It can be seen in the SEM result that at this time there are coexistence of well reacted area (the bright part on the left side) and Areas that have not yet fully reacted (non-glossy part on the right side) on the YBCO film surface. Meandering boundaries of these two areas is an indication of the presence of transient liquid phase when the temperature is near 800°C.

According to the results above, it can be deduced that the reaction between BaCO₃ and other oxides does not produce YBCO directly, but to form intermediate products including liquid phase, which reacts with other reactants to form YBCO crystals in later process. This is consistent with the studies on phase evolution in FF-MOD method by Vermeir et al. [13]. In their study BaCO₃ is regarded to involve in the following reactions:

\[
\text{BaCO}_3 + \text{CuO} \rightarrow \text{BaCuO}_2 + \text{CO}_2 \uparrow \quad (2)
\]

\[
2\text{BaCuO}_2 + \text{CuO} \rightarrow \text{liquid} + x\text{O}_2 \uparrow \quad (3)
\]

\[
\frac{1}{2} \text{Y}_2\text{O}_3 + \text{liquid} \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6-x} \quad (4)
\]

**Figure 4.** SEM results on samples quenched in different temperature
(a) 640°C  (b) 660°C  (c) 680°C  (d) 720°C  (e) 760°C  (f) 800°C
The evolution YBCO phase are basically follow the rules below: 1) YBCO phase begins to form near 680 °C; 2) YBCO phase experienced an evolution of “no YBCO phase - only the presence of YBCO(103) - the coexistence of YBCO(103) and YBCO(00l) - only YBCO (00l)” in crystallization process; 3) Corresponding to the phase evolution pattern of YBCO, the surface morphology also experienced an evolution of “irregular grains – only polycrystalline YBCO crystals – coexistence of polycrystalline and oriented YBCO crystals – only oriented YBCO crystals” in crystallization process. This indicates that, initially YBCO film appear as polycrystalline gains at 680°C. Afterwards, the polycrystalline YBCO grains reorganizes to orientated ones at higher temperature, and the liquid phase generated in intermediate process is involved in this reorganization process.

Samples prepared by the complete pyrolysis, crystallization and oxygen annealing process were measured by SEM and PPMS system, results was calculated from the equation (1). As shown in Figure 5, the surface of the film is basically flat and composed of plate-like c-axis oriented grains. There are also nanoscale pores on the sample surface, we think it is caused by the roughness of the substrate itself ($R_a = 2.0 \text{nm}$, 5x5 μm scale) and the interface reaction at the CeO$_2$ / YBCO interface [16] since such morphology cannot be observed in the YBCO films deposited on LAO single crystal substrates. And as shown in figure 6,YBCO film prepared on technical substrates has $J_c = 0.8 \text{MA/cm}^2$ (77K, 0T, with 190nm thickness).

4. Conclusion
In this paper, YBCO thin films were prepared technical substrates by FF-MOD method. Phase evolution of BaCO$_3$ and YBCO phases during crystallization process was studied by quenching and characterizing samples at different temperatures.

The ATR-FT-IR, SEM and two-dimensional XRD characterization of samples quenched at different temperatures indicated that the reaction of BaCO$_3$ with oxides of Y and Cu elements will not directly generate YBCO, but experience some intermediate process. The formed YBCO crystal are randomly oriented at 680°C, and then gradually reorganize into textured crystals at higher temperature. Transient liquid phase generated in the intermediate process is involved in the YBCO reorganization process.

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