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Facile and efficient preparation of high-performance $REBa_2Cu_3O_{7-x}$ superconducting films through a novel fluorinated solution route

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ABSTRACT

$REBa_2Cu_3O_{7-x}$ (RE = Y, Gd, Yb) superconducting films were prepared through an advanced low-fluorine solution route. The precursor solution was prepared using fluorine-free copper and barium salts, and fluorine-contained rare earth salts. Metal fluorides and oxides were formed as intermediate phases in the precursor films, which were pyrolyzed at 400–500 °C. After reacting with water gases during the firing process at 800 °C, the fluorides were transformed into the oxides, finally leading to the formation of superconducting $REBa_2Cu_3O_{7-x}$ (REBCO) phases. Due to the low-content of fluorine in the solution, high-rate production of REBCO films could be realized using this low-fluorine solution method. All the REBCO films had a good out-of-plane texture with a high critical transition temperature of more than 90 K and a critical current density of more than 2 MA/cm^2.

1. Introduction

Chemical solution deposition (CSD) shows a great potential in the preparation of a large number of inorganic oxide films, such as transparent conducting films, ferroelectric, dielectric films, etc. [1,2]. Recently, CSD method has been extensively used to produce large-scale, biaxially-textured REBCO superconducting films [3,4]. Unfortunately, the traditional chemical solution routes using fluorine-free precursors for the synthesis of REBCO films easily result in the formation of $BaCO_3$ or some other undesired phases in the final films, leading to the poor superconductivity [5]. Fluorine-contained chemical solution routes using trifluoroacetates (TFA) as precursors have attracted much interest due to its high reproducibility in the fabrication of high-quality REBCO films [6–8]. The formation of BaF_2 intermediate phase rather than $BaCO_3$ during the pyrolysis process can finally alleviate the formation of carbon-related phases, leading to the phase-pure REBCO film with high-performance.

It is reported that the fluorine-content in the precursor solution had great influences on the film processing and even final film superconductivity [9]. Thus, the optimization of the precursor solution takes great importance for the commercialization of the REBCO tapes. Using traditional All-TFA solution (prepared using Y, Ba, and Cu trifluoroacetates), a long pyrolysis time of 10–20 h was needed to alleviate the bubbling evidence of harmful fluorinated gases so as to obtain the film with a smooth surface. In fact, the decomposition of Cu-TFA salts results in the copper oxide rather than CuF_2 [10]. Therefore, the fluorine-reduced solution without Cu-TFA can be adopted to prepare REBCO films with smooth surface. Based on this idea, an "Advanced TFA-MOD" process (a fluorine-reduced solution process) was put forward by Izumi et al. [11]. Nowadays, Advanced TFA-MOD developed by ISTEC (International Superconductor Technology Center, Japan) provided YBCO film with a high critical current of 470 A cm^{-1} W^{-1} after multiple coating and calcination [11]. Another kind of fluorine-reduce solution process was put forward by Chen [12] and Yoo et al. [13]. This kind of solution, named as low-fluorine solution, was prepared using Ba-TFA and fluorine-free Y and Cu salts as precursors. This kind of technique showed great potential in future commercial application due to their unique of fast preparation of high-J_c YBCO tapes [9,14].

However, the low-fluorine solution commonly contains amine-related groups, which always degrade the solution stability. An advanced low-fluorine solution without amine-groups was then developed. This kind of advanced low-fluorine solution contains Y-TFA, and fluorine-free barium and copper salts. The formation mechanism of BaF_2 rather than $BaCO_3$, however, remains unclear. In this paper, the formation and removal mechanism of fluorides during the heat treatment process were discussed. Moreover, we extended the advanced low-fluorine solution process from YBCO to some other REBCO films ($GdBa_2Cu_3O_{7-x}$ (GdBCO) and $YbBa_2Cu_3O_{7-x}$ (YbBCO) films). REBCO films with improved superconductivity were obtained using a modified pyrolysis process.

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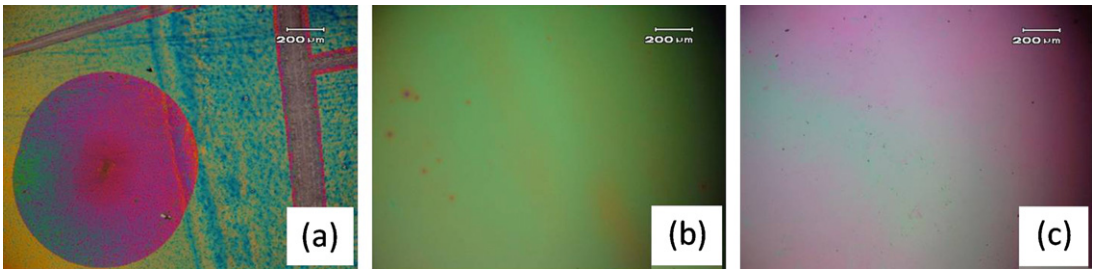

Fig. 1. Surface morphologies of different precursor films pyrolyzed using the heating rate of 5 °C/min from 200 °C to 310 °C; (a) All-TFA solution derived precursor film pyrolyzed at 310 °C; (b) advanced low-fluorine solution derived precursor film pyrolyzed at 310 °C; (c) advanced low-fluorine solution derived precursor film pyrolyzed at 450 °C.

2. Results and discussion

Fig. 1 shows the macroscopic surfacial morphologies of different pyrolyzed films observed by the optical microscopy. For the gel film derived from All-TFA solution, it was reported that a smooth surface without any large pores could only be obtained when the heating rate was lower than 0.5 °C/min from 200 °C to 300 °C. On the contrary, the evidence of bubbling and cracks with a size of more than 200 μm was observed in the film, which was decomposed at 5 °C/min (Fig. 1(a)). In the fluorine-free CSD process, although CO_2 gas was generated during the pyrolysis process, the bubbling due to the CO_2 generation could not be observed, even at the higher heating rate [15]. Therefore, it could be concluded that the bubbling and cracks in the All-TFA film were due to the generation of fluorinated gases such as CF_3COF, COF_2, HF, etc. [16,17]. However, using the advanced low-fluorine solution, the amount and the releasing rate of generated fluorinated gases is greatly decreased. In this case, the abrupt release of the detrimental fluorinated gases could be avoided, and thus the gas bubbling and cracks could be effectively prevented. This assumption was verified by our current research. Using a heating rate of 5 °C/min, the obtained precursor films had a smooth surface without any cracks and bubbling, as shown in Fig. 1(b) and (c).

In the fluorine-free solution route, $BaCO_3$ was easily formed as an intermediate phase, which would be left in the final REBCO film as impurity phase, degrading the film superconductivity. In the All-TFA solution route, $BaCO_3$ was avoided by forming BaF_2 as the intermediate phase in the precursor film. In the advanced low-fluorine solution, the Ba-salt and Cu-salt were fluorine-free, and only RE-TFA was the fluorine-containing salt. It should also be noted that fluorine-free RE-salts such as RE-acetates or some other RE-carboxylates were not dissolved in the methanol without the help of the amine groups. This indicated that in the advanced low-fluorine solution, the dissociated TFA ions should be coordinated with rare-earth, rather than Ba and Cu ions. Then, could BaF_2 rather than $BaCO_3$ be formed in the precursor film? To clarify this, different precursor solutions were used to prepare a series of precursor films. X-ray diffraction experiments were carried out on the precursor films, which were pyrolyzed at different temperatures, as shown in Fig. 2. At 275 °C, the gel film derived from the fluorine-free Cu solution was transformed to the CuO film (Fig. 2a). The barium solution processed film was still amorphous after being pyrolyzed at 325 °C (Fig. 2b). The fluorine-containing Y-solution and the fluorine-free Ba-solution were then mixed, and the corresponding gel films were pyrolyzed at 325 °C. Interestingly, $Ba_{1-x}Y_xF_{2+x}$ phase (BYF), i.e. an extensive solid of BaF_2 and YF_3 [18,19], were formed, as shown in Fig. 2c. This indicated that the decomposition of Y-TFA not only resulted in the formation of YF_3, but the formation of BaF_2 by the decomposed TFA group reacting with the amorphous Ba-salt. Correspondingly, the precursor film derived from the advanced YBCO low-fluorine solution mainly contained CuO and BYF phases after pyrolysis at 350 °C (Fig. 2d) and 450 °C (Fig. 3a). The elements of Gd and Yb had the similar properties as the Y element. The same intermediate phases of corresponding $Ba_{1-x}RE_xF_{2+x}$ fluorides ($Ba_{1-x}Yb_xF_{2+x}$ and $Ba_{1-x}Gd_xF_{2+x}$) and CuO were also found in the precursor films derived from YbBCO and GdBCO solutions, as shown in Fig. 3b and c, respectively. Yb_2O_3 was also detected in the YbBCO precursor film. For YBCO and GdBCO precursor films, the existence of Y_2O_3 and Gd_2O_3 could not be confirmed, because they might exist in amorphous state or as nanocrystal grains, which kept silent to XRD.

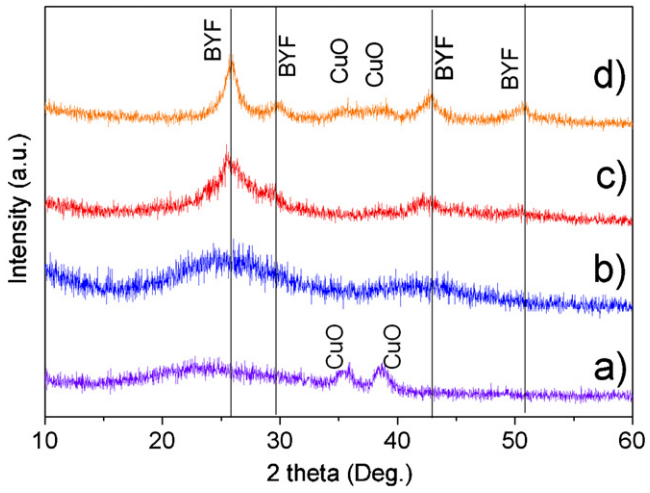

Fig. 2. XRD patterns for different precursor films derived from: (a) the fluorine-free Cu solution, pyrolyzed at 275 °C; (b) the fluorine-free Ba solution, pyrolyzed at 325 °C; (c) the mixture solution of Y and Ba solution, pyrolyzed at 325 °C; (d) the advanced YBCO low-fluorine solution, pyrolyzed at 350 °C.

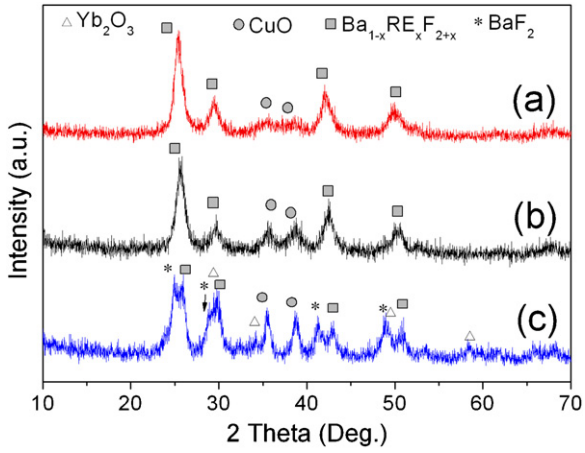

Fig. 3. XRD patterns for different precursor films derived from: (a) YBCO solution; (b) GdBCO solution; and (c) YbBCO solution. All the film were pyrolyzed at 450 °C.