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Improvement of production rate of YBCO coated conductors fabricated by TFA-MOD method

K. Nakaoka*, M. Yoshizumi, Y. Usui, T. Izumi, Y. Shiohara

Superconductivity Research Laboratory, ISTEK, 4-1-1, Minamihashimoto, Chuo-Ku, Sagami-hara-Shi, Kanagawa-Ken, 252-0253, Japan

Abstract

The metal-organic deposition (MOD) method using trifluoroacetate (TFA) salts is considered to be an effective method for inexpensively fabricating $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) coated conductors with high critical current density property. The long-length TFA-MOD YBCO coated conductors have been fabricated by multi-turn reel-to-reel system. Increasing the thickness per single coating in the multi-turn reel-to-reel system is a cost-effective technique for fabrication of the precursor films in the calcination process since it reduces the number of coatings and shortens the processing time. In this work, we have developed a new starting solution consisting of non-fluorine salts of yttrium propionate and copper 2-ethylhexanoate with focusing on increasing the thickness per single coating for a high-rate fabrication of the YBCO coated conductors by the TFA-MOD method. The critical thickness per single coating of the precursor film fabricated from the new starting solution was improved to $0.44 \mu\text{m}/\text{coat}$. Furthermore, the addition of diacetoneacrylamide in the new starting solution increased the critical thickness per single coating to $0.79 \mu\text{m}/\text{coat}$. High critical current of $791 \text{ A}/\text{cm}$ -width with high critical current density of $2.7 \text{ MA}/\text{cm}^2$ was obtained using the new starting solution with diacetoneacrylamide at the thickness per single coating of $0.49 \mu\text{m}/\text{coat}$.

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Keywords: YBCO; TFA-MOD method; thick film

1. Introduction

The metal-organic deposition (MOD) process using the metal salts of trifluoroacetic acid (TFA) could easily yield $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) films with high critical current density (J_c) performance [1,2]. Additionally, since the TFA-MOD method does not require a high-vacuum system, it is expected to be suitable for large-scale production of YBCO coated conductors with low-cost. In our previous work, we have fabricated long-length TFA-MOD YBCO coated conductors with high critical current (I_c) property using the starting solution that consisted of yttrium- and barium trifluoroacetates and copper 2-ethylhexanoate by multi-turn reel-to-reel system [3]. The calcination process was still the rate-limiting process in the TFA-MOD method. Increase of thickness per single coating is an effective approach to accelerate the calcination process, however, it easily causes J_c reduction due to bubbling, cracking, and delamination. The rate of the gas generation, which is determined by the amount of fluorine element in the starting solution, the molecular weight of the metal-organic compounds, thickness per single coating, and the heating rate, affects the film quality (bulk density, uniformity etc.) [4]. The further reduction of the fluorine content in the starting solution is one possible way to increase the thickness per single coating with maintaining high J_c performance. Therefore, we have investigated to replace the yttrium trifluoroacetate by fluorine free yttrium salt at the starting solution. A new starting

* Corresponding author. Tel.: +81-44-850-1611; fax: +81-44-850-1613.
E-mail address: knakaoka@istec.or.jp

solution using fluorine free yttrium salt of yttrium propionate, which could be calcined with thicker single coatings than the conventional starting solution, was developed for the improvement of the production rate of the calcination process by the TFA-MOD method in this study.

2. Experimental

The starting solutions were prepared by dissolving yttrium, barium, and copper salts in the organic solvent with a total metal concentration of 1.3 mol/L [5]. In this study, two kinds of starting solutions were prepared: (1) conventional starting solution consisting of yttrium and barium trifluoroacetates, and copper 2-ethylhexanoate; (2) new starting solution consisting of yttrium propionate, barium trifluoroacetate, and copper 2-ethylhexanoate. Furthermore, diacetoneacrylamide was used as the additive agent.

These starting solutions were deposited on the CeO₂ (Pulsed laser deposition) buffered LaMnO₃ (RF sputter)/MgO (Ion beam assisted deposition)/Gd₂Zr₂O₇ (Ion beam sputter)/Hastelloy™ [6] substrates (10×50 mm²) by the dip-coating method. The dip-coating was performed at room temperature by immersing the substrates vertically in the starting solution and withdrawing them at a constant rate. The film thickness was controlled by withdrawal rate. These samples were applied to the two stages of heat treatments for conversion to YBCO as described elsewhere [5].

The film thickness was obtained from the inductively coupled plasma spectrometry (ICP) analysis as the average YBCO film thickness after conversion. The surface morphology observation of the precursor films were performed by the optical microscopy installed with a charge coupled device video camera. The thermal decomposition behavior of metal complexes was evaluated by thermogravimetric and differential thermogravimetric (TG-DTG) analysis. The thickness distribution of the precursor films was directly observed along transversal direction by the cross-sectional scanning electron microscope (SEM) observation. The I_c of the YBCO films were measured by a conventional four-probe DC transport method at 77 K in self-fields with the 1 μ V/cm criterion.

3. Results and Discussion

The precursor films were fabricated from the conventional and the new starting solutions by a single dip-coating procedure. Figure 1A shows the relationship between the withdrawal rate and the final film thickness estimated by ICP analysis. The film thickness increased with increasing the withdrawal rate in both solutions. In the case of the conventional solution, the defect was observed in the precursor films with film thickness over 0.27 μ m. On the other hand, the defect was not observed up to 0.42 μ m in the precursor films fabricated from the new solution. The observation of the surface morphology of the precursor films was performed by optical microscopy. Figure 1B shows the surface morphology of the precursor films fabricated from the conventional solution with different film thickness: (a) 0.22 μ m (withdrawal rate of 1.5 m/h); (b) 0.37 μ m (withdrawal rate of 3.5 m/h). There were no defects in the precursor film with the film thickness of 0.22 μ m. The circular-shaped defects were observed in the precursor film with film thickness of 0.37 μ m. The defect is thought to occur due to the gas bubbling which might be related to rate of gas generation in the precursor films and/or shrinkage accompanying thermal decomposition of metal-organic compounds during the calcination process [4].

Figure 2 shows the TG-DTG curves of powder of (a) yttrium trifluoroacetate and (b) yttrium propionate complexes. The mass loss in the temperature range up to about 100°C is attributed to dehydration in both samples. The peak values of DTG curves of yttrium trifluoroacetate and yttrium propionate were 15.9 and 7.3 %/min, respectively. These results probably indicate that the gas generation and/or shrinkage rate during the calcination process in the case of using new starting solution is milder than that of using conventional solution. Therefore, the suppression of defect was realized probably due to decrease in the gas generation and/or shrinkage rate during the calcination process.

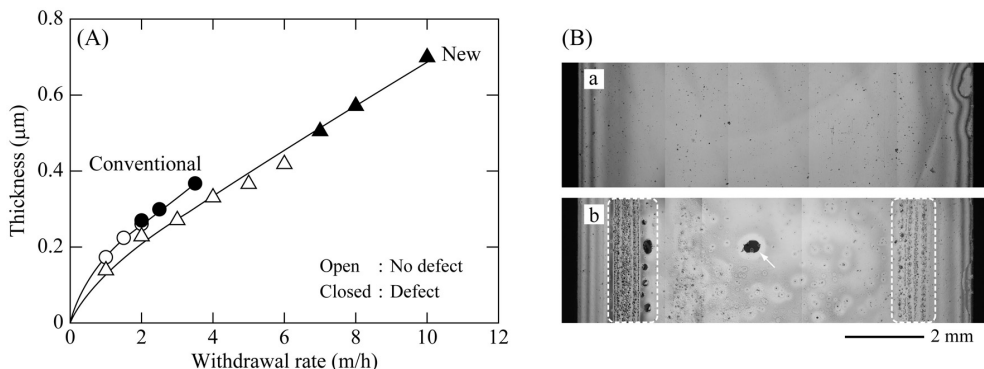


Fig. 1. (A) Relationship between the withdrawal rate of the dip-coating using the conventional and the new starting solution and the film thickness per single coating. (B) Optical microscopic images of the precursor films fabricated from the conventional starting solution at the withdrawal rate of (a) 1.5 and (b) 3.5 m/h.

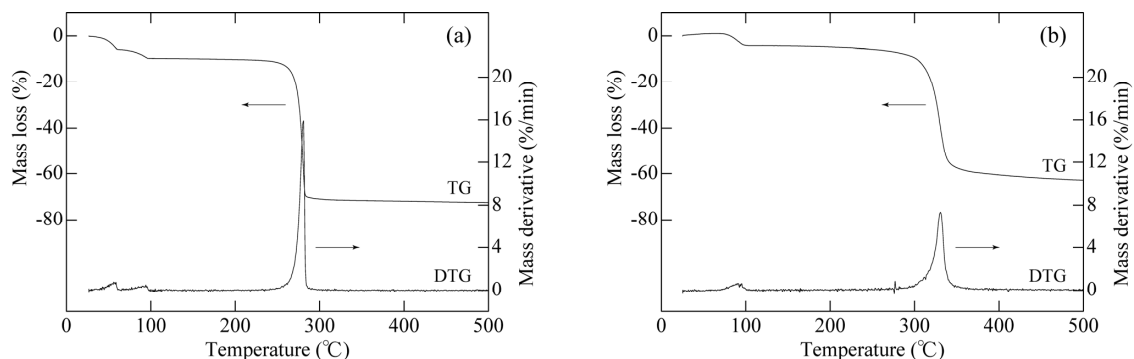


Fig. 2. TG-DTG curves of powder of (a) yttrium trifluoroacetate and (b) yttrium propionate. The heating rate was 2°C/min.

The critical film thickness per single coating of precursor film was improved from 0.22 to 0.42 μm by using new starting solution. However, the defect of cracks was occurred in the precursor films with the film thickness over 0.42 μm . In dip-coating, film thickness distribution in transverse direction is un-uniform [7]. The thickness distribution of the precursor films derived from new starting solution in transversal direction was observed by cross-sectional SEM observation. Figure 3 shows the thickness distribution of precursor films with different film thickness: (a) withdrawal rate of 3.0 m/h (no defect); (b) withdrawal rate of 8.0 m/h (defect). The thickness of the precursor film fabricated at the withdrawal rate of 3.0 m/h increases from zero to maximum within 0.70 mm (maximum film thickness: 1.13 μm) from the side edge and then decreases down to the flat film thickness at 1.50 mm (central flat region film thickness: 0.72 μm). The thickness ratio of the projected region to the central flat region was 1.57. In the precursor film fabricated at withdrawal rate of 8.0 m/h, the film thickness increases from zero to maximum within 1.80 mm (maximum film thickness: 3.07 μm) from the side edge and then decreases down to the flat film thickness at 3.05 mm (central flat region film thickness: 1.54 μm). The crack of precursor film was observed at 2.02 mm from the side edge. The thickness ratio of the projected region to central flat region was 1.99. The film thickness distribution in transverse direction could become un-uniform by increasing the precursor film thickness per single coating. The crack observed in the precursor film fabricated at withdrawal rate of 8 m/h was owing to large thickness distribution in transverse direction. J.T. Dawley *et al.* [8] reported the successful shortening of the calcination process by using diacetoneamine-containing solution, so we examined the amino group-containing compounds as an additive agent for further improvement of the thermal decomposition process in calcination and/or the thickness distribution of the precursor film. Diacetoneacrylamide was selected as additive agent.

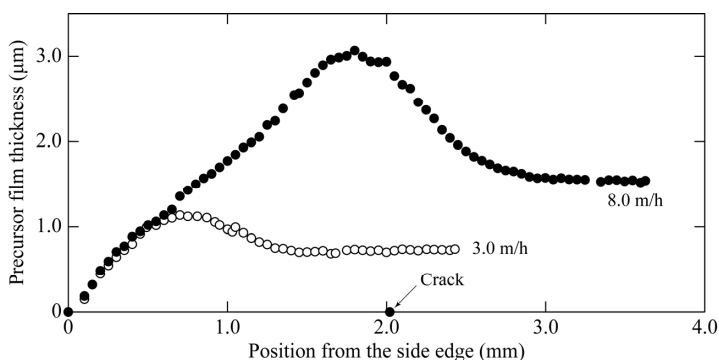


Fig. 3. Thickness distribution of the precursor film in transversal direction. The precursor films were fabricated from new starting solution at the withdrawal rate of 3.0 (\circ) and 8.0 m/h (\bullet).

Figure 4 shows the relationship between the withdrawal rate of dip-coating and the thickness of precursor films fabricated from the new starting solutions with and without diacetoneacrylamide. The critical film thickness per single coating of precursor film was significantly improved from 0.42 to 0.79 μm by addition of diacetoneacrylamide. However, the mechanism of this result is not yet clear and needs further study. In this new starting solution containing diacetoneacrylamide, it is necessary to investigate the thermal decomposition behavior and observe the thickness distribution of the precursor films. The superconducting properties of YBCO films fabricated from the new starting solution with diacetoneacrylamide were investigated.

The dipping condition and superconducting properties of YBCO films are shown in Table 1. High I_c value of 791 A/cm-width with high J_c value of 2.7 MA/cm² was obtained in the 2.91 μm thick YBCO film fabricated at the thickness per single coating of 0.49 μm (withdrawal rate: 5.0 m/h). The technical cost of the fabrication of the YBCO layer was reduced about 34% by applying this condition to the current reel-to-reel system. The J_c value decreased to 1.8 MA/cm² when the YBCO film fabricated at the thickness per single coating of 0.77 μm (withdrawal rate: 10 m/h). This degradation of J_c value might be caused by un-optimized condition of crystallization process.

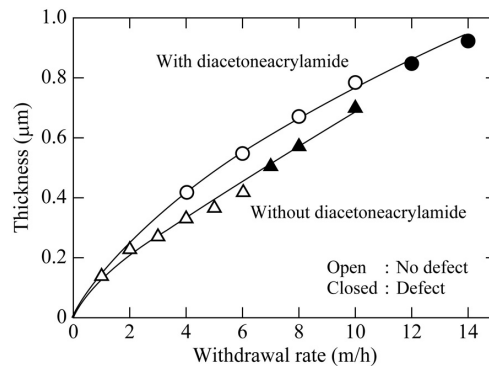


Fig. 4. Relationship between the withdrawal rate of the dip-coating using the new starting solution with and without diacetoneacrylamide and the film thickness per single coating.

Table 1. The dipping condition and superconducting property of YBCO films fabricated from new starting solution with diacetoneacrylamide.

Number of coating	Withdrawal rate (m/h)	Thickness per single coating (μm)	Total thickness (μm)	I_c (A/cm-w)	J_c (MA/cm ²)
6	5	0.49	2.91	791	2.7
3	10	0.77	2.30	405	1.8

4. Conclusion

We have developed a new starting solution containing fluorine free salt of yttrium propionate, barium trifluoroacetate and copper 2-ethylhexanoate focusing on enhancement of the production rate in the calcination process. The critical thickness per single coating of precursor film was significantly improved from 0.22 to 0.79 $\mu\text{m}/\text{coat}$ by using the new starting solution with diacetoneacrylamide. High I_c value of 791 A/cm-width with high J_c value of 2.7 MA/cm² was obtained in the YBCO film fabricated on CeO₂ buffered LaMnO₃/MgO/Gd₂Zr₂O₇/HastelloyTM substrates using the new starting solution at the thickness per single coating of 0.49 $\mu\text{m}/\text{coat}$.

Acknowledgements

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