

Improvement of production rate by modified TFA-MOD starting solution

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Abstract—We developed a new TFA-MOD starting solution using F-free salt of Y, TFA salt of Ba and Cu-Octylate for application to the coating / calcination process and discussed several issues by using the Multi-turn (MT) Reel-to-Reel (RTR) system calcination furnace for the purpose of high throughput without degradation of the properties. The coating system was improved for uniform deposition qualities in both longitudinal and transversal directions.

YBCO films using the new starting solution at the traveling rate of 10m/h in coating / calcination by the MT-RTR calcination furnace showed the values of the critical current density of 1.5MA/cm² as thick as 1.5μm at 77K under the self fields after firing for crystallization.

I. INTRODUCTION

YBCO coated conductors (CCs) with high critical current density (J_c) under the self-fields as well as the external magnetic field would be expected for application to some electric power devices such as power cables, Superconducting Magnetic Energy Storage (SMES) and transformers. A 56m long tape of YBCO derived from the TFA-MOD process was developed to have the J_c value of 250A/cm-width using a conventional starting solution including TFA salt of Y, TFA salt of Ba, naphthenic acid of Cu with the Ba-deficient composition (Y:Ba:Cu=1:1.5:3). However, there were two serious problems to be solved including the generation of tar during the long calcination process and different qualities in the different batch solutions since the naphthenic acid is extracted from the natural petroleum source. So, we developed a new starting solution including TFA salt of Y, TFA salt of Ba, Cu-Octylate with the Ba-deficient composition (Y:Ba:Cu=1:1.5:3) which is called as “the advanced solution”. Although the advanced solution solved the above-mentioned problems, there is still an issue for higher speed production without degradation of properties for realizing the lower cost. In order to improve the production speed, another starting solution was developed based on the similar concept to the advanced solution, i.e. reduction of the fluorine contents in the solution [4], which is called as the further advanced starting solution (F-advanced). The films derived from the F-advanced solution revealed the high J_c values of over 2.5MA/cm² in the short specimens.

In this study, we investigated the influences of the maximum temperature and the heating rate in the calcination heat treatment step in order to apply the F-advanced solution to the MT-RTR calcination furnace.

II. EXPERIMENTAL PROCEDURE

The starting solutions were prepared by dissolving F-free salt of Y for the F-advanced solution or TFA salt of Y for the advanced one, TFA salt of Ba and Cu-Octylate with a cationic ratio of Y : Ba : Cu = 1:1.5:3 into the organic solvent. The starting solution was coated on the CeO₂ buffered IBAD-Gd₂Zr₂O₇ / Hastelloy C276 substrates by the dip coating method followed by heating up to 420-510 °C in an O₂ gas flow using the MT-RTR calcination furnace which has a typical temperature gradient of 25°C/min. The film thickness per single coating was controlled by viscosity of the solution and the traveling rate of the films. Finally these samples were heated to 740-800°C in the mixed humid (P(H₂O)=15vol.%) gas flow of argon and oxygen with P(O₂) = 10⁻⁴-10⁻³ atm. The final thickness of the YBCO superconductor films was about 1.0-1.6μm. The precursor films and the crystallized YBCO films were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Transmission Electron Microscopy (TEM). In addition, the chemical composition analysis of these films and the film thickness were measured by Inductively Coupled Plasma (ICP). The critical current (I_c) of the crystallized films was measured at 77 K under the self-fields by the DC four-probe method with the criterion of voltage of 1μV/cm.

III. RESULTS AND DISCUSSION

Figure 1 shows the properties of the YBCO films derived from the advanced solution and the F-advanced one for different traveling rates of coating and calcinations from 2m/h to 10m/h. The films from the F-advanced starting solution maintained the high J_c values up to the high speed traveling rate of 10m/h in the coating and calcination step, while the films from the advanced one revealed degradation of J_c values with increasing the rate. We found that the F-advanced solution was appropriate to fabricate superconducting films with high J_c values at the high traveling rate of 10m/h for coating and calcination.

Table 1 shows the growth conditions and the superconducting properties of the films from both the advanced and the F-advanced solutions. It was found that there are large differences in the properties (J_c) for the heating rates of 2 and 70°C/min in the crystallization step especially in the films coated and calcined at the high traveling rate. The precursor films coated and calcined at the traveling rate of 10m/h using the F-advanced solution showed the high J_c values of about 2.0MA/cm² after firing at the low heating rate of 2°C/min in the crystallization step. However, the J_c value was degraded to the 0.7MA/cm² in the film fired at the heating rate of 70°C/min in the crystallization step. Additionally, in the case of the advanced solution, the films were not uniformly coated on the substrate at the traveling rate of 10m/h in the coating and calcination step, which

resulted in low J_c values after firing for crystallization. As the next step, we have tried to develop new process conditions for F-advanced solutions which could realize high superconducting properties with high speeds both in the coating / calcination and in the crystallization step.

Figure 2 shows the relationship between J_c values in the films from the F-advanced solution and the maximum temperature in the calcination step (T_{max}^C) at the traveling rate of 10m/h in coating and calcination after firing at the heating rate of 70°C/min. As a result, the J_c values of the films with T_{max}^C of 500°C were over 1.6MA/cm² at the high heating rate of 70°C/min in the crystallization step.

Figure 3 shows the J_c values of the films derived from the F-advanced solution with different heating rates from 2°C/min to 70°C/min in the crystallization step. The precursor films calcined by the heating profiles with different temperatures (T_{max}^C) of 420°C and 500°C were used in this experiments. The films with the T_{max}^C of 420°C, revealed the high J_c value of about 2.0MA/cm² under limited conditions only at the low heating rate of 2°C/min in the crystallization step. The precursor films calcined by the T_{max}^C of 500°C, however, showed J_c values of about 1.6MA/cm² in the entire range of the heating rates from 2°C/min to 70°C/min in the crystallization step. It could be explained that the properties were degraded at the high heating rate in the crystallization step due to the residue of fluoride, carbide and organic compounds in the calcined films.

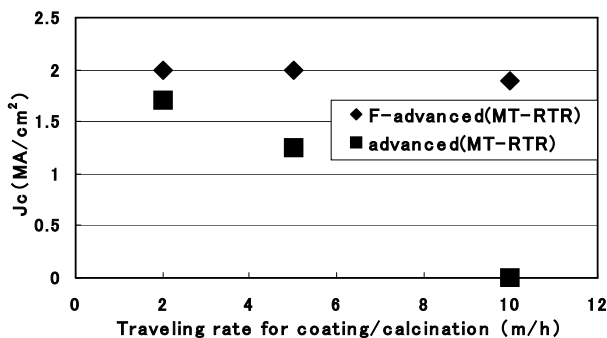


Fig.1 Properties of the YBCO films derived from the advanced solution and the F-advanced one at different traveling rates in the coating and calcination step

TABLE I

GROWTH CONDITIONS AND SUPERCONDUCTING PROPERTIES OF THE FILMS FORMED FROM BOTH THE ADVANCED AND F-ADVANCED SOLUTIONS

Starting Solution	Viscosity of Solution (cp)	Traveling rate for Coating/calcination (m/h)	Heating for Crystallization (°C/min)	J_c (MA/cm ²) @77K
advanced	27	2	2	1.7
			70	1.7
	15	5	2	1.6
			70	1.25
	10	10	2	0
F-advanced	15	10	2	2.0
			70	0.7

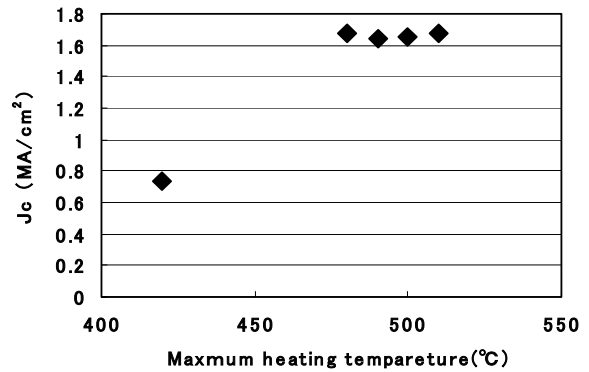


Fig.2 Relationship between the J_c values in the films from the F-advanced solution and the maximum temperature in the calcination step (T_{max}^C) at the traveling rate of 10m/h in coating and calcination after firing at the heating rate of 70°C/min.

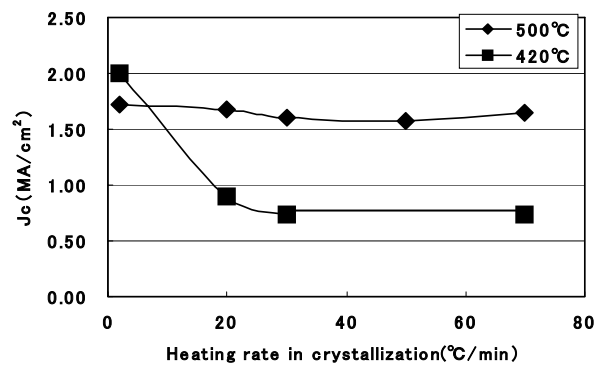


Fig.3 J_c values of the films derived from the F-advanced solution with different heating rates from 2°C/min to 70°C/min in the crystallization step

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