Progress in R&D for YBCO Coated Conductors by TFA-MOD Processing

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Abstract. Recent progress in the research and development of the TFA-MOD processing for the coated conductors is reviewed. For the higher Ic performance, process conditions such as heating rate and water vapor inlet temperature in the calcination step and heating rate and water vapor pressure in the crystallization step have been optimized to obtain YBCO films with good crystallinity. Consequently, a high Ic value of 431A/cm-w was achieved by the combination of the above optimized conditions with the use of highly textured CeO₂ cap layered substrates. Forwards the effort for long tape fabrication with high production rate, the multi-turn system for coating and calcination step was developed. Additionally, the reel-to-reel system for the crystallization step was developed for the longer tape, and a 25m long YBCO tape with a reasonable end-to-end Ic value of 100A, which corresponds to 2500Am as a product of Ic x L, was obtained by the above continuous system. For the higher production rate in the crystallization step, it was confirmed that optimization of the processing parameters such as high water partial pressure, high diffusion constants due to low total pressure, and a high gas flow rate affects the YBCO growth rate.

1. Introduction

YBa₂Cu₃O₇₋ₓ (YBCO) coated conductors are highly a promising candidate for high performance wires which could be used at the liquid nitrogen temperatures. In order to obtain high critical currents (Ic) for the future applications of YBCO coated conductors, thicker films maintaining a high critical current density (Jc) value are required on a long tape. In addition, a high production rate and low cost should be satisfied. Metal organic deposition (MOD) of precursor solutions containing metal trifluoroacetates (TFA) is an attractive process to produce YBCO films since we could easily attain a high Jc by a simple process in a non-vacuum low cost manner. We have fabricated YBCO films with a high Ic value of 413A (77K, self field) and Jc value of 2.0 MA/cm² by the TFA-MOD process using a multi-coating method[2]. YBCO films with higher Ic values, however, should be developed for applications, requiring thicker films while maintaining the high Jc value. For the long tape processing,
a reel-to-reel (RTR) system is applied both in the calcination and the crystallization steps. In this system, it is important to obtain the uniform reaction not only along the long direction but also along the width in the furnace. Higher production rate is also one of the important issues to be solved in the development of the long-tape processing. In order to obtain thicker films for high I_c, the number of the calcination steps in the multi-coating method has to be increased in the coating and the calcination steps. On the other hand, the long annealing time due to increase of the film thickness makes the effective production rate low in the crystallization step. Equation (1) shows a simple equation for the production rate in the RTR system,
\[ V = \frac{(L \cdot R)}{d} \]
where, \( V \), \( L \), \( R \) and \( d \) are tape traveling rate, furnace length, YBCO growth rate and film thickness, respectively. According to equation (1), a higher production rate is realized by longer \( L \), higher \( R \), and decrease of \( d \) derived from the higher \( J_c \) value.

In this paper, our recent progress in R&D by the TFA-MOD process is reviewed.

2. High Performance
The optimization of the growth conditions both for the calcination and the crystallization steps has been studied to obtain high \( J_c \) values. Concerning the calcination step, the influence of the water vapor inlet temperature and the heating rate on the microstructure and the superconducting characteristics were investigated. The water vapor inlet temperature was changed from 25°C to 350°C in the calcination step. Figure 1 shows the influence of the water vapor inlet temperature on the \( J_c \) values. The \( J_c \) value decreased drastically when the water vapor was started to be introduced at the lower temperature than 200°C to 400°C under the heating rate of 2°C/min. From the SEM observations of the films calcined with different inlet temperatures of 100°C and 350°C, as shown in figure 2, the film with the low inlet temperature in calcinations leads to the growth of the misoriented YBCO grains in the films after the crystallization step. The relationship between the heating rate in the calcination step and \( J_c \) was also investigated. It was clarified that the low heating rate in the calcination step is suitable for attaining high \( J_c \) values, since the misoriented grains could be suppressed by reduction of Cu-segregation, pores and wavy interfaces in the precursor[2].

The effect of \( P_{H_2O} \) in the crystallization step on the microstructure and \( J_c \) of YBCO films was investigated for the different \( P_{H_2O} \)'s in the range 0.8-25% at a heating rate of 25°C /min. The YBCO films with 1.2 µm in thickness were utilized in this investigation. The \( P_{H_2O} \) dependence of \( J_c \) is shown in Figure 3. The \( J_c \) value increased with increasing \( P_{H_2O} \) from 0.8 to 13.5%. Films crystallized at 13.5% of the \( P_{H_2O} \) condition showed a maximum \( J_c \) value of 2.1 MA/cm². \( J_c \) decreased as \( P_{H_2O} \) increased over the values larger than 20%. In order to clarify the \( J_c \) behavior on \( P_{H_2O} \), we have investigated the microstructure of the film in detail using TEM. Figure 4 shows cross-sectional TEM images of YBCO films crystallized at \( P_{H_2O}=2.1 \), 13.5 and 20%, respectively. In these pictures, bright regions were confirmed to be pores in the YBCO films by energy dispersive X-ray spectroscopy (EDS) analysis. As shown in Figures 4(a) and (c), large pores are observed in the low-\( J_c \) films. In contrast, there are few large pores in the film treated in 13.5% of \( P_{H_2O} \). Small pores are dispersed in this film. The pore formation mechanism was discussed in our previous report[3]. The large pores may cause local reduction of the cross section for the current path and additionally introduction of concentration of electric fields. It was confirmed, furthermore, from the surface observation that cracks were formed in the films crystallized at \( P_{H_2O}>20% \), in contrast to the films crystallized under the conditions with \( P_{H_2O}<13.5% \). Consequently, both crack generation and large pore formation cause a \( J_c \)-decrease of the YBCO films. Figure 3 suggests the existence of a critical \( P_{H_2O} \), for crack-free films with high \( J_c \) in the same film thickness. Then, the relationship between the conditions of the crack formation in YBCO films was investigated including the film thickness and \( P_{H_2O} \) in the crystallization conditions. As seen in Figure 5, the \( P_{H_2O} \) depends strongly on the film thickness and decreases with increasing film thickness. It was also confirmed that the lower heating rate is effective for suppressing cracking especially in the thicker films.
The higher superconducting performance could be expected in thicker YBCO films using the above mentioned optimum information both in the calcination and the crystallization steps. Consequently, the high Ic value of 431A/cm-w was achieved by the combination of the above optimized growth conditions with use of highly textured CeO2 cap layered substrates.

3. Long Tape processing

In our previous attempts to fabricate long tapes, it was difficult to obtain a uniform reaction not only along the long direction but also along the width[2]. Through the investigation of the reasons for the low uniformity, it was found that bowing of the metal substrate along the width direction could lead to a non-uniform gas flow above the film. It could cause non-uniform gas boundary layer thickness and distribution of the related growth rates. In order to prevent the bowing of the substrate, a GZO layer was deposited on the reverse side by the PLD process, since it was clarified that the bowing is caused by the existence of a GZO layer on the Hastelloy. The curve almost disappeared by control of the thickness of the reverse sided GZO layer. On the other hand, a stagnant gas region in the furnace could be a reason not only for the low growth rate but for the long transient in the initial and final reaction regions, which leads to non-uniformity in the long direction. The simulation of the growth and the gas flow in the furnace was studied to solve the problem of the gas stagnant region. From the calculations, several solutions were suggested. A higher gas flow condition during the growth of the YBCO layer was applied in this study. Relatively uniform performance was obtained in the 4m-long YBCO tape with a high Ic value of about 250A. Furthermore, a 25m-long tape was fabricated as shown in Fig.6. The end-to-end Ic value of 100A was realized in the 25m tape, which corresponds to 2500Am as a product of Ic x L values.

4. High YBCO Growth Rate Processing

As mentioned above, in order to accomplish a higher Jc value and R, understandings of the YBCO growth mechanism and its control are important. We have proposed a one-dimensional analysis for
YBCO growth during the crystallization step, considering both diffusion in the gas boundary layer and the growth kinetics at the precursor/YBCO interface in this process[4],

$$R = \frac{M_j}{4M_{Y123}} \frac{D_g}{g} \sqrt{KX_{H_2O}}$$

(2)

where $M_j$ and $M_{Y123}$ are the molar concentrations in the gas region and the YBCO layer, and $D_g$ is the diffusivity in the gas region, $g$ is the diffusion boundary thickness, $K$ is the equilibrium constant for the reaction to produce the YBCO phase, $X_{H_2O}$ is the molar flux of the $H_2O$ in the inlet gas, respectively. The YBCO growth model was in good agreement with the experimental results by using the same order of the equilibrium constant as the reported one, and the growth rate was proportional to the square root of $P_{H_2O}$. Moreover, it was suggested that the processing parameters such as diffusivity and gas flow rate could affect the growth rate as well from the above analysis. A diffusivity is generally in inversely proportion to the total pressure, $P_t$. A gas flow rate is in proportion to the gas flow volume, $V_{gas}$. Then, $P_t$ and $V_{gas}$ dependences on the YBCO growth rate, $R$, were investigated on the RTR system. Figure 7 shows the $V_{gas}$ dependences on $R$ and $I_c$ performance. As shown in figure 7, the $R$ value increased with increasing $V_{gas}$ maintaining the same $I_c$ value. The $P_t$ dependence on $R$ and $I_c$ performance are shown in figure 8. It is likely that $R$ increases with the lower $P_t$ maintaining the same $I_c$ value. Finally, it was confirmed that the higher $R$ could be achieved by the crystallization conditions of higher $P_{H_2O}$, higher $D_g$, and higher $V_{gas}$.

5. Conclusion

Process conditions such as heating rate and water vapor inlet temperature in the calcination step and heating rate and water vapor pressure in the crystallization step have been optimized for the higher $I_c$ performance. The process parameters such as low $\Delta \phi$ values of the CeO$_2$ buffer layer for the higher $J_c$ of YBCO film, the high water partial pressure, high diffusion constants due to the low total pressure, and the high gas flow rate affect the YBCO growth rate in the reel-to-reel system.

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References

[1] R. Teranishi, J. Matsuda, K. Nakaoka, H. Fuji, Y. Aoki, Y. Kitoh, T. Iizumi, Y. Yamada, Y. Shiohara, IEEE Trans. Appl. Supercond., 15, 2 (2005) 2663
[2] T. Iizumi, H. Fuji, Y. Aoki, R. Teranishi, K. Nakaoka, J. Matsuda, Y. Kitoh, Y. Yamada, Y. Shiohara, Y. Iijima, T. Saitoh, T. Gotoh, A. Yoshinaka, A. Yajima IEEE Trans. Appl. Supercond., 15, 2 (2005) 2743
[3] J. S. Matsuda, Y. Tokunaga, R. Teranishi, H. Fuji, A. Kaneko, S. Asada, T. Honjo, A. Yajima, Y. Iijima, T. Saitoh, T. Iizumi, Y. Shiohara. Physica C, Vol. 412-414 (2004) 890
[4] T. Honjo, Y. Nakamura, R. Teranishi, H. Fuji, J. Shibata, T. Iizumi, Y. Shiohara, IEEE Trans. Appl. Supercond, 13, 2 (2003) 2516