Optimization of interim heat-treatment condition on TFA-MOD process for fabrication of $Y_{0.77}Gd_{0.23}Ba_2Cu_3O_y$ coated conductors with BaHfO$_3$

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Abstract. We have optimized the interim heat-treatment (IHT) time in trifluoroacetate based metal organic deposition process on fabrication of the BaHfO$_3$ (BHO) doped $Y_{0.77}Gd_{0.23}Ba_2Cu_3O_y$ (YGdBCO) coated conductor (CC) in order to further improve the in-field critical current density ($J_c$) performance. The in-field $J_c$ values of 0.6 μm-thick BHO doped YGdBCO CCs increased with increasing the IHT time within 90 min. The highest critical current density ($J_c$) value of 0.86 MA/cm$^2$ at 77 K in 3 T ($B//c$) was obtained for 0.6 μm-thick BHO doped YGdBCO CC with IHT time of 90 min. CCs with IHT time shorter than 90 min had relative low in-field $J_c$ performance but high self-field $J_c$ performance. It can be caused by the insufficient transformation to BaF$_2$ in IHT which is a reason for the relatively large BHO particles. In the case of applying IHT for longer time than 90 min, coarsening of CuO particles in precursor films was suggested and degradation of self- and in-field $J_c$ performances were observed.

1. Introduction

The metal organic deposition (MOD) process using metal trifluoroacetates (TFA) has been recognized as a process for cost-effective and suitable for large-scale production to fabricate REBa$_2$Cu$_3$O$_y$ (RE: rare-earth element, REBCO) coated conductors (CCs) with high-performance in a self-field. However, it had been lower comparing with the CCs by the vapor process in a magnetic-field. On the other hand, low cost CCs with high in-field superconducting performance have been required for electric power applications such as magnetic resonance imaging, motors, generators, and accelerators.

The standard heat-treatment procedure of the conventional TFA-MOD process consists of calcination and crystallization steps. The calcination step is performed at low-temperature for thermal decomposition of a starting solution to an amorphous precursor phase. The amorphous precursor films are crystallized to REBCO phase at high-temperature during the crystallization step. In order to improve the in-field critical current density ($J_c$) performance of BaMO$_3$ (M: metal element, BMO) doped REBCO CCs, we have modified the heat-treatment procedure of TFA-MOD process and proposed new heat-treatment step, which was called as “interim heat-treatment (IHT)”, introduced between the calcination and the crystallization steps [1-3]. The IHT gives improving homogeneous dispersion of the finer BMO particles and improving the in-field $J_c$ performance of BMO doped REBCO CCs. The fundamental analysis of IHT was previously reported [3]. We found that the IHT is
the process to transfer from BaF$_2$−(Y,Gd)F$_3$ solid solution (SS) to BaF$_2$ and Y$_2$O$_3$ which is the necessary condition of BMO nucleation. However, the IHT conditions (temperature, holding time and atmosphere etc.) have not been optimized.

In this paper, we have optimized the IHT conditions, particularly IHT time, for further improvement of in-field $J_c$ performance of BaHfO$_3$ (BHO) doped Y$_{0.77}$Gd$_{0.23}$Ba$_2$Cu$_3$O$_y$ (YGdBCO) CCs.

2. Experimental

The starting solution was obtained by dissolving and mixing yttrium and gadolinium propionates, Bartrifluoroacetate, copper 2-ethylhexanoate, and tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) hafnium with the ratio of Y : Gd : Ba : Cu : Hf equal to 0.77 : 0.23 : 1.60 : 3.00 : 0.10 in 1-methoxy-2-propanol [4].

The starting solution was controlled with the total metal (excluding hafnium) concentration of 0.45 mol/L. The starting solution was deposited by spin-coating onto CeO$_2$ (pulsed laser deposition) buffered LaMnO$_3$ (radio frequency sputter deposition)/MgO (ion beam-assisted deposition)/Y$_2$O$_3$ (ion beam sputter deposition)/Gd$_2$Zr$_2$O$_7$ (ion beam sputter deposition)/Hastelloy$^{\text{TM}}$ substrates (33 mm in length and 10 mm in width) at 4800 rpm for 20 s. This spin-coated sample was placed on an alumina plate which was inserted in an electric tube furnace and then subjected to a heat-treatment consisting of a series of calcination, IHT, and crystallization steps. The calcination was performed by heating up to 500°C at the heating rate of 10°C/min in O$_2$ atmosphere at atmospheric pressure. To prepare thicker precursor films, we repeated the spin-coating and the calcination 20 times. Subsequently, the thick precursor films were applied to the IHT and crystallization steps for conversion to the superconducting phase. The heating profile for the crystallization step with IHT step is shown in figure 1. The IHT and crystallization processes were applied under a mixed gas atmosphere of humid Ar and O$_2$ (total pressure: 30 kPa, partial pressure of H$_2$O: 1.7 kPa, partial pressure of O$_2$: 0.04 kPa). Holding time in the IHT step was varied 0 to 240 min and holding time in the crystallization step was 80 min. Consequently, 0.6 μm-thick BHO doped YGdBCO films were obtained. The thickness of the films was determined by a cross-sectional scanning electron microscopic observation. A quenched sample during the IHT step was prepared by removing from the electric tube furnace and immediately dropping onto a thick copper block at room temperature. This quenched sample preparation was done within 10 sec. The BHO doped YGdBCO films were oxygen annealed at 500°C under oxygen pressure of about 200 kPa for 1 h.

X-ray diffraction (XRD) analyses were carried out with Cu Kα radiation. The critical current was measured at 77 K under self- and magnetic field by the direct-current four-probe transport technique with a criterion of 1 μV/cm.

![Figure 1. Heating profile of crystallization step with interim heat-treatment.](image)

3. Results and Discussion

XRD analyses of quenched samples after holding for 0, 30, 60, 90, 120, 180, and 240 min at 580°C during the IHT step were performed to investigate the microstructure evolution in precursor films. Figure 2 shows the XRD patterns of quenched samples scanned in ranges of 2θ from 20 to 32° and from 34 to 54°. Four broad diffraction peaks excluding the peaks from the CeO$_2$ buffered LaMnO$_3$/MgO/Y$_2$O$_3$/Gd$_2$Zr$_2$O$_7$/Hastelloy$^{\text{TM}}$ substrate (2θ ~ 22.4 and 46.0°; LaMnO$_3$, 2θ ~ 29.7°; Gd$_2$Zr$_2$O$_7$, 2θ ~ 43.4°; Hastelloy$^{\text{TM}}$) were observed at 2θ ~ 25.6, 29.8, 42.6 and 50.5° for quenched sample with IHT time of 0 min. These four diffraction peaks correspond to a BaF$_2$−(Y,Gd)F$_3$ solid solution (SS) phase [3]. BaF$_2$ and (Y,Gd)F$_3$ are present as a SS phase in the precursor films as
As the IHT time increased, all four diffraction peaks moved to lower 2θ angles and shifted to 

\[ 2θ \sim 24.8, 28.8, 41.1 \text{ and } 48.7^\circ \]

for the quenched sample with IHT time of 240 min. The diffraction peaks of 2θ ~ 24.8, 28.8, 41.1 and 48.7° are indexed to the (111), (200), (220) and (311) planes of pure BaF₂ phase, respectively, which indicates that the BaF₂−(Y,Gd)F₃ SS to pure BaF₂ phase transformation occurred during the IHT. Therefore, the basic reaction is proposed as follows [3];

\[
2(Y,Gd)F_3 (\text{in BaF}_2−(Y,Gd)F_3 \text{ SS}) + 3\text{BaF}_2 (\text{in BaF}_2−(Y,Gd)F_3 \text{ SS}) + 3\text{H}_2\text{O (g)} \\
\rightarrow (Y,Gd)_2\text{O}_3 + 3\text{BaF}_2 + 6\text{HF (g)}.
\] (1)

Additionally, new XRD diffraction peak of CuO(1̅11) around 2θ = 35° was confirmed in quenched samples with long IHT time of over 90 min.

The IHT time dependence of the diffraction peak position of BaF₂−(Y,Gd)F₃ SS (2θ ~ 25.6°) in quenched samples is shown in figure 3. It can clearly be seen from this figure that the peak of BaF₂−(Y,Gd)F₃ SS moved to the position of pure BaF₂ (2θ ~ 24.8°) with increasing the IHT time. Furthermore, transformation reaction from BaF₂−(Y,Gd)F₃ SS phase to pure BaF₂ phase was found to achieved at IHT time of around 60 min for the samples having a final thickness of about 0.6 μm. Figure 4 shows the relationship between the XRD peak intensities of (1̅11) plane of CuO phase in quenched samples and IHT time. The diffraction peak of CuO(1̅11) plane was observed in the quenched samples with IHT time of more than 90 min. As for the diffraction peak of CuO(1̅11) plane observed at IHT time
of longer than 90 min, the diffraction peak intensity increased with increasing IHT time, which might be due to coarsening of CuO particles.

The influence of IHT time on $J_c$ performance of BHO doped YGdBCO CCs was investigated. Figure 5 shows the IHT time dependence of the $J_c$ values at (a) 77 K in self-field and (b) 77 K in 3 T $(B//c)$ for BHO doped YGdBCO CCs. High $J_c$ values of above about 4.5 MA/cm$^2$ were obtained at 77 K in self-field (a) for the CCs with IHT time of 90 min or less. On the other hand, the $J_c$ values decreased with increasing of the IHT time longer than 90 min. The $J_c$ values at 77 K in 3 T $(B//c)$ (b) increased with increasing IHT time until 90 min. The increment of in-field $J_c$ performance is believed from the results of the fine dispersion of BHO particles in the CCs due to the progress of IHT reaction (reaction 1). The BHO particles can be nucleated at low-temperature because the necessary condition of transformation from BaF$_2$–(Y,Gd)F$_3$ SS to BaF$_2$ is almost completed during the IHT step. The low-temperature nucleation and growth might affect to the suppression of growth of the BHO particles due to low diffusivity. The highest $J_c$ value of 0.86 MA/cm$^2$ at 77 K in 3 T $(B//c)$ was obtained for CC with IHT time of 90 min. The $J_c$ values decease with increasing the IHT time over 90 min, as well as behaviour of $J_c$ performance at 77 K in self-field (a). The degradation of $J_c$ performance of CCs with IHT time of more than 90 min might be related to the coarsening of CuO particles in the precursor films. Although the mechanism has not yet been elucidated, it is known that there is compositional segregation within the thickness of once layer in multilayered precursor films [5-7]. Rupich et al reported that a copper-rich region is presented between the individual layers in the multilayered precursor film and the epitaxial growth of YBCO is partially disrupted as it crosses the copper-rich interface, which leads to the $J_c$ degradation of the YBCO film [6, 7]. In our previously study, Y, Gd, Ba elements segregate at the lower part of each layer, and in contrast, Cu element at the upper part [5]. Therefore, this degradation of $J_c$ performance of CCs with long IHT time might be due to formation of blocking layers of coarsened CuO, which inhibits the epitaxial growth of REBCO phase during the crystallization step, in the precursor film by coarsening of CuO particles.

4. Conclusion
We have optimized the IHT time on fabrication of the 0.6 μm-thick BHO doped YGdBCO CCs for further improving the in-field $J_c$ performance. The in-field $J_c$ value of CCs was improved with

![Figure 4. Relationship between the XRD peak intensities of (111) plane of CuO phase in quenched samples and IHT time.](image)

![Figure 5. IHT time dependence of the $J_c$ values at (a) 77 K in self-field and (b) 77 K in 3 T $(B//c)$ for BHO doped YGdBCO CCs.](image)
increasing the IHT time within 90 min. The highest $J_c$ value of 0.86 MA/cm$^2$ at 77 K in 3 T ($B//c$) was obtained for CC with IHT time of 90 min. In the case of applying IHT for longer time than 90 min, the degradation of $J_c$ performance of CCs was confirmed. Furthermore, coarsening of CuO particles in the precursor films was observed. The degradation of $J_c$ performance of CCs with long IHT times might be due to formation of blocking CuO layers, which inhibits the epitaxial growth of REBCO phase during the crystallization step, in the precursor film by coarsening of CuO particles. In the optimization of IHT time, we found the existence of lower and upper limits of IHT time, which are determined by the required time for complete transformation to pure BaF$_2$ phase (reaction 1) and the formation of the blocking layer to the epitaxial growth of REBCO phase due to coarsening of CuO, respectively.

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