Superconducting properties of (Y\(_1-x\)Eu\(_x\))Ba\(_2\)Cu\(_3\)O\(_y\)-coated conductors prepared via trifluoroacetate–metalorganic deposition

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Abstract. In order to investigate the effect of the partial substitution of Y by Eu on the superconducting properties of REBa\(_2\)Cu\(_3\)O\(_y\) (RE: rare earth) films, we fabricated trifluoroacetate–metalorganic deposited Y\(_{1-x}\)Eu\(_x\)Ba\(_2\)Cu\(_3\)O\(_y\) (\(x=0.1, 0.23, 0.3, 0.4, 0.5\)) films on metallic substrates with optimal crystallization conditions. The optimized crystallization conditions for fabricating Y\(_{1-x}\)Eu\(_x\)Ba\(_2\)Cu\(_3\)O\(_y\) coated conductors with high x composition are relatively high crystallization temperature and low oxygen pressure comparing with YBa\(_2\)Cu\(_3\)O\(_y\). The films with high x values exhibit a high critical temperature, irreversible fields, and high critical current density in the high-magnetic region at 77 K. However, the inferiority on the critical current density of the films with high x in self and low fields at 77 K is not necessary conformed. This behavior might be explained by the influence of the melt-growth mode in the film with high x.

1. Introduction

REBa\(_2\)Cu\(_3\)O\(_y\) [REBCO; rare-earth (RE) elements=Y, Gd, Eu etc.] films deposited on flexible and lightweight metallic substrates, manufactured by the ion-beam assisted deposition (IBAD) or on the rolling-assisted biaxial textured substrates, often referred to as coated conductors (CCs), hold promise for various industrial applications such as in generators, transmission, cables, and superconducting magnetic energy storage. REBCO films can be manufactured with several techniques, including the pulsed laser deposition (PLD) [1, 2], the metalorganic chemical vapor deposition (MOCVD) [3], the reactive co-evaporation (RCE) [4], and the metalorganic deposition (MOD) [5, 6]. Among these deposition techniques, the trifluoroacetate (TFA)-based MOD (TFA-MOD) is notably economical because it does not require a high-vacuum system. Although YBa\(_2\)Cu\(_3\)O\(_y\) (YBCO) CCs fabricated by TFA-MOD possess good superconductivity, having a high critical temperature (\(T_c\)) and critical current density (\(J_c\)) in an external magnetic field, significant improvements to the in-field \(J_c\) are still required.

Much work in this direction has focused on partially substituting or displacing the Y in these films with other RE elements. Partial substitution of Y by Sm has been shown to drastically increase the in-field \(J_c\) in PLD-Y\(_{2/3}\)Sm\(_{1/3}\)Ba\(_2\)Cu\(_3\)O\(_y\), which resulted in an in-field \(J_c\) of 0.06 MA/cm\(^2\) at 75.5 K and a magnetic field of 5 T applied parallel to the c-axis of the films which related with the crystallographic c-axis [7]. This value is three times higher than that of YBCO. Goswami et al. reported that PLD-Y\(_{1-x}\)Eu\(_x\)Ba\(_2\)Cu\(_3\)O\(_y\) film has higher in-field \(J_c\) than unsubstituted YBCO because the Eu-substituted
material has dense c-axis-correlated defects that result in an improvement of flux-pinning properties in weak magnetic fields [8]. In the case of fabrication with TFA-MOD, Y_{0.77}RE_{0.23}Ba$_2$Cu$_3$O$_y$ (RE=Sm or Gd) CCs have high in-field $J_c$ compared with YBCO CCs [9]. Although SmBCO in bulk material has a higher maximum $T_c$ than GdBCO at ~94 K [10], the in-field $J_c$ properties of Y$_{0.77}$Gd$_{0.23}$Ba$_2$Cu$_3$O$_y$ are superior to those of Y$_{0.77}$Sm$_{0.23}$Ba$_2$Cu$_3$O$_y$ in the coated conductors. It might be caused by the difficulty to control of the substitution of Ba by Sm sites [11]. According to the above-mentioned knowledge, Eu was selected as a substituting element for Y because of its high $T_c$ but little substitution into Ba site [12-14]. In this work, in order to investigate the effect of the partial substitution of Y by Eu on superconducting properties, we used the TFA-MOD process to fabricate Y$_{1-x}$Eu$_x$Ba$_2$Cu$_3$O$_y$ ($x=0.1$, 0.23 0.3, 0.4, 0.5) CCs with optimal crystallization conditions.

2. Experimental

Y$_{1-x}$Eu$_x$Ba$_2$Cu$_3$O$_y$ (Y$_{1-x}$Eu$_x$BCO) films were grown from organic metal solutions including Y-propionate, Eu-propionate, Ba-trifluoroacetate, and Cu-2-ethylhexanoate [15, 16] with a molar ratio of Y:Eu:Ba:Cu =1-x:0.3:1.5:3 onto the following substrates: laminated structure of PLD-CeO$_2$, Y$_2$O$_3$, LaMnO$_3$, IBAD-MgO, GaidZr$_2$O$_7$, and Hastelloy C276. The solution, with a metal-ion concentration of 1.2 mol/L, was deposited on a CeO$_2$-buffered substrate by the spin-coating technique. The coated films were then decomposed onto an amorphous precursor film by heating them to 500°C in humid flowing oxygen gas with a water-vapor partial pressure $[P(H_2O)]$ of 3.2 kPa and a water inlet temperature of 400°C. This coating/calcination decomposition process was repeated to obtain a final thickness of about 0.5 μm. The precursor films were then heated to their maximum temperature ($T_{max}$) in a humid mixed argon and oxygen atmosphere with $P(H_2O)$ of 3.2 kPa. The optimized conditions had been investigated for each composition with $T_{max}$ of 700°C–820°C and oxygen partial pressure $[P(O_2)]$ ranging 0.01–0.05 kPa. Here, the optimized condition for compositied CCs was meant for the highest self-field $J_c$ at liquid nitrogen temperature. The crystallized films were then annealed at 500°C under 200 kPa for 60 min in O$_2$ followed by furnace cooling to room temperature.

The microstructure of the crystallized Y$_{1-x}$Eu$_x$BCO films was observed using a scanning electron microscope (SEM). The self-field $J_c$ values were measured in 1-cm-wide films by the standard four-probe DC transport method under liquid-nitrogen temperature with the criterion in voltage of 1μV/cm. For resistivity and in-field $J_c$ measurements, the films were patterned into ~55μm-wide strips by the laser etching. These measurements were performed with the standard four-probe method using a Quantum Design Physical Properties Measurement System that can generate a magnetic field of up to 9 T. $T_c$ and irreversibility field ($B_{irr}$) were determined using a 0.01-$\rho_N$ sample, where $\rho_N$ is the normal-state resistivity.

3. Results and Discussion

To find optimized conditions in crystallization step for Y$_{1-x}$Eu$_x$BCO CCs, we examined the properties of the REBCO films fabricated under crystallization conditions of $T_{max}$ of 700°C–820°C and $P(O_2)$ of 0.01–0.05 kPa. It was found that as $x$ increases in Y$_{1-x}$Eu$_x$BCO CCs, suitable $T_{max}$ increases and $P(O_2)$ decreases. This can be explained by the high peritectic temperature of EuBCO than that of YBCO [17]. To clarify the effect of substitution by Eu in the TFA-MOD REBCO CC, we compared Y$_{0.77}$Eu$_{0.23}$BCO CCs with Y$_{0.77}$Gd$_{0.23}$BCO CCs formed under each optimal crystallization conditions. As a result, Y$_{0.77}$Eu$_{0.23}$BCO revealed a higher $T_c$ (=91.1 K) than Y$_{0.77}$Gd$_{0.23}$BCO ($T_c$=90 K) even with the same substitution quantity ($x=0.23$).

We also measured the self-field transport properties with different quantities of substituted Eu. Figure 1 plots the substitution quantity ($x$) dependence of $T_c$ and self-field $J_c$ ($J_c^{x-1}$) at 77 K for Y$_{1-x}$Eu$_x$BCO CCs. The $T_c$ values of Y$_{1-x}$Eu$_x$BCO CCs increase from 88.5 K to 91.9 K as $x$ increases, indicating that Eu substitution amount can make $T_c$ higher. The improvement in $T_c$ after partial substitution of Y by Eu is attributable to the higher maximum $T_c$ in EuBCO than that in YBCO [12]. It also suggests that the YBCO and EuBCO phases are uniformly distributed in the Y$_{1-x}$Eu$_x$BCO matrix. Moreover, we can see
Figure 1. The dependence of $T_c$ (left axis) and $J_{c,s.f.}$ (right axis) on quantity of substituted Eu ($x$) at 77 K for $Y_{1-x}Eu_xBCO$ CCs.

Figure 2. The dependence of $B_{intr}$ on temperature at $B \parallel c$ for in $Y_{1-x}Eu_xBCO$ CCs with $x=0$, 0.23, 0.4, and 0.5.

Figure 3. The dependence of $J_c$ at 77 K and $B \parallel c$ on applied magnetic field for $Y_{1-x}Eu_xBCO$ CCs with $x=0$, 0.23, 0.4, and 0.5. The inset shows the magnetic-field dependence ($B < 2$ T) of $J_c$ for $Y_{1-x}Eu_xBCO$ CCs with $x=0$, 0.23, 0.4, and 0.5.

that the $T_c$ values of $Y_{1-x}Eu_xBCO$ CCs do not increase linearly with Eu substitution amounts, which may imply the necessity of further optimization in the condition of the oxygen-annealing. On the other hand, the $J_{c,s.f.}$ in $Y_{1-x}Eu_xBCO$ CCs decreases slightly with increasing $x$. For small amounts of substitution, such as $x \leq 0.1$, the $J_{c,s.f.}$ values were in the range 4.9–5.2 MA/cm$^2$ at 77 K. For high substitutions amounts, such as $x=0.5$, the $J_{c,s.f.}$ values drop by about 10%. In general, $J_c$ depends strongly on $T_c$. Therefore, the degradation of $J_{c,s.f.}$ for high $x$ was unexpected because $T_c$ had been improved.
In-field transport properties under the same conditions were also measured. Figure 2 shows the temperature dependence of $B_{irr}$ at $|B|c$ in $Y_{1-x}Eu_xBCO$ CCs with $x=0$, 0.23, 0.4, and 0.5. As for $|B|/c$, the CCs with high substitutions of Eu exhibit higher $B_{irr}$ than those with smaller amounts of Eu, indicating that the differences in $B_{irr}$ values are related to differences in $T_c$. Figure 3 showed the $J_c$ values at 77 K and $|B|/c$ against the external magnetic field for $Y_{1-x}Eu_xBCO$ CCs with $x=0$, 0.23, 0.4, and 0.5. The inset of Figure 3 shows the magnetic field ($B < 2$ T) dependence of $J_c$ for $Y_{1-x}Eu_xBCO$ CCs with $x=0$, 0.23, 0.4, and 0.5. $Y_{1-x}Eu_xBCO$ CCs have lower $J_c$ than unsubstituted YBCO CCs (those with $x=0$) when $B < 2$ T. Additionally, the $J_c$ of $Y_{1-x}Eu_xBCO$ CCs with high $x$ under a low magnetic field does not necessarily improve, as shown the inset of Figure 3. On the other hand, $Y_{1-x}Eu_xBCO$ CCs with high $x$ have high $J_c$ under a high magnetic field than the CCs with small $x$. The enhancement of $J_c$ in a high magnetic field for the CCs substituted with large amounts of Eu should be a result of the improvement of $B_{irr}$ and $T_c$.

To understand the self-field and low-field $J_c$ behaviors in the Eu-substituted CCs, we observed the microstructure using SEM as shown in Figure 4. The size and the number of pores in the matrix decreases with increasing Eu substitution amount, whereas the amount of solidified liquid phase increases on the surface of the superconducting layers (see white arrow in Figure 4) accordingly. The difference in microstructures and the behaviors of electro-magnetic properties in the CCs with different substitution quantities could be explained as follows: In the case of small $x$ at low $T_{max}$ and high $P(O_2)$ in optimized crystallization conditions, pores result from the reactions of the non-superconducting phase entrapped in the matrix during the epitaxial growth, since this solid-state reaction causes volume shrinkage [18]. With high $x$ at high $T_{max}$ and low $P(O_2)$ in optimized crystallization conditions, the solidified liquid phase might be ejected because of the dominance of the melting layer at the growth front of the superconducting layer. It results in higher crystallinity and the suppression of pore formation since the intermediate phase in front of the growing interface is easier to dissolve in the liquid phase, which lead to the reduction of the trapped particles. However, the segregation of the residual phase at the grain boundary in the melt-growth mode can be assumed because the high purify grain can be grown. The segregation at the grain boundaries might degrade the grain-to-grain connectivity in the superconducting layer although the potential of the grain itself is higher due to its high crystallinity. Moreover, the agglomeration and/or coarsening CuO grains (see in Figure 4 (b)) might be cause by the influence of the melt-growth mode. Thus, the influence of the melt-growth mode might make the self-field and low-field $J_c$ in CCs lower with high amounts of Eu substitution although $T_c$, $B_{irr}$ and $J_c$ in the high magnetic field regions are higher.

4. Conclusion

In order to investigate the effect of the partial substitution of Y by Eu on superconducting properties in the REBCO coated conductors, we fabricated $Y_{1-x}Eu_xBa_2Cu_3O_y$ ($x=0.1, 0.23 0.3, 0.4, 0.5$) films on metallic substrates by the TFA-MOD method under optimal crystallization conditions for each composition. As $x$ increases in $Y_{1-x}Eu_xBCO$ CCs, suitable $T_{max}$ increases and $P(O_2)$ decreases. The $T_c$ values of $Y_{1-x}Eu_xBCO$ CCs increase with increasing $x$, which shows the highest $T_c=91.9$ K in this study.
However, the $J_{c}$ in $Y_{1-x}$Eu$_x$BCO CCs decreases slightly with increasing $x$. The CCs with high substitutions of Eu show higher $B_{irr}$ than those with smaller amounts of Eu due to the improvement of $T_{c}$. On the other hand, $Y_{1-x}$Eu$_x$BCO CCs with high $x$ have high $J_{c}$ under high magnetic field regions than the CCs with small $x$, although the improvement of $J_{c}$ in low magnetic field for the CCs with high $x$ does not confirmed. From microstructures, melt-growth mode in $Y_{1-x}$Eu$_x$BCO CCs with high $x$ conditions appears. The residual segregation at the grain boundary which can be assumed in the melt-growth mode might degrade the grain-to-grain connectivity in the superconducting layer. It seems to be a reason for lower $J_{c}$ in low magnetic field including self-field.

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