Flux pinning properties of REBa$_2$Cu$_3$O$_y$ films fabricated by a metal-organic deposition using metal-naphthenates and 2-ethylhexanates

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Abstract

We studied the relationship between microstructure and flux pinning properties of REBCO films fabricated by a MOD technique using metal-naphthenate and 2-ethylhexanate (2-EH) solutions. 2-EH-(Sm$_{0.3}$, Ho$_{0.7}$)Ba$_2$Cu$_3$O$_y$ film achieved high $J_c$ of 2.19 MA/cm$^2$ at 77 K due to introduction of effective pinning sites. GdBa$_2$Cu$_3$O$_y$ film prepared using complex solutions (CS) obtained high $J_c$ of 30 MA/cm$^2$ at 4.2 K in spite of having low $J_c$ at 77 K. Anomalous temperature dependence of $J_c$ was also observed for CS-GdBa$_2$Cu$_3$O$_y$ film. It is speculated that lower-$T_c$ regions act as strong pinning centers in the CS-GdBa$_2$Cu$_3$O$_y$ film by comparison analysis with flux pinning for NbTi with artificial pins.

1. Introduction

REBa$_2$Cu$_3$O$_y$ (REBCO) coated conductors have been under development by many research institutes for high engineering $J_c$ and high magnetic field applications at liquid nitrogen temperature [1-3]. Several kinds of fabrication method, such as pulsed laser deposition (PLD), chemical vapour deposition (CVD) and metal-organic deposition (MOD) have been studied actively [4-8]. Among them, MOD technique may be more suitable for mass production of REBCO coated conductors than others because this technique is a non-vacuum and cost effective process [9]. Especially a MOD technique using metal-naphthenates (MN) and 2-ethylhexanates (2-EH) has an advantage to avoid the use of fluorine during the process [10]. In this paper we studied the relationship between microstructure and flux pinning properties of several kinds of REBCO films fabricated by the MOD technique using MN and 2-EH solutions. (Sm$_{0.3}$, Ho$_{0.7}$)Ba$_2$Cu$_3$O$_y$ film prepared by 2-ethylhexanates achieved maximum $J_c$ of 2.19 MA/cm$^2$ at 77 K under self-field due to introduction of effective pinning sites. GdBa$_2$Cu$_3$O$_y$ film prepared by 2-ethylhexanates showed high $J_c$ of 0.92 MA/cm$^2$ at 77 K and 3.3 MA/cm$^2$ at 4.2 K under self-field due to its excellent crystallization. On the other hand, GdBa$_2$Cu$_3$O$_y$ film prepared by complex solutions (CS) achieved much
higher $J_c$ of 30 MA/cm$^2$ at 4.2 K in spite of having low $J_c$ of 0.51 MA/cm$^2$ at 77 K. Anomalous temperature dependence of $J_c$ was also observed for CS-GdBa$_2$Cu$_3$O$_y$ film. It suggests that strong pinning centers are induced into CS-GdBa$_2$Cu$_3$O$_y$ film at low temperatures. It is speculated that lower-$T_c$ regions act as effective pinning centers in the CS-GdBa$_2$Cu$_3$O$_y$ film by comparison analysis with flux pinning for NbTi with artificial pinning centers.

2. Experimental detail

Several kinds of superconducting films of REBCO were fabricated by the MOD technique. The solutions were prepared by mixing metal MN salts and 2-EH salts or only 2-EH salts with a nominal atomic ratio of Gd: Ba: Cu = 1: 2: 3, or of Sm: Ho: Ba: Cu = 0.3: 0.7: 2: 3. The solutions were coated on substrates of LaAlO$_3$ single crystal (100) by spin coating at 3,500 rpm for 30 sec. And then the films were dried at 120°C for 30 min, and calcined at 450 or 600°C for 20 or 30 min in air. This process was repeated 3-5 times. The precursor films were fired at 850-860°C for 30 min in a nitrogen (N$_2$) gas flow containing partial oxygen of 10$^{-6}$ atm at a flowing rate of 0.1 l/min$^{-1}$. These films were annealed 350 or 500°C for 2 hour in a oxygen (O$_2$) flow at a flowing rate of 0.1 l/min$^{-1}$, and finally the REBCO films were obtained. Table 1 shows the fabrication process of the films. CS-Gd film was fabricated using complex solution mixed MN and 2-EH. 2-EH-Gd film was fabricated using 2-EH solution. 2-EH-GP film was fabricated using solution mixed 2-EH and colloidal solutions with Pt. 2-EH-HS film was fabricated using 2-EH solution with a nominal atomic ratio of Sm: Ho: Ba: Cu = 0.3: 0.7: 2: 3.

<table>
<thead>
<tr>
<th>Films</th>
<th>Solutions</th>
<th>Composition</th>
<th>Calcination temperature[°C]</th>
<th>Firing temperature[°C]</th>
<th>Firing rate[°C/min]</th>
<th>O$_2$ annealing temperature[°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-Gd</td>
<td>CS</td>
<td>Complex solution GdBa$_2$Cu$_3$O$_y$</td>
<td>450</td>
<td>850</td>
<td>10</td>
<td>500</td>
</tr>
<tr>
<td>2-EH-Gd</td>
<td>2-EH</td>
<td>2-ethylhexanates GdBa$_2$Cu$_3$O$_y$</td>
<td>450</td>
<td>860</td>
<td>7.5</td>
<td>350</td>
</tr>
<tr>
<td>2-EH-GP</td>
<td>2-EH</td>
<td>2-ethylhexanates GdBa$_2$Cu$_3$O$_y$ +Pt</td>
<td>600</td>
<td>860</td>
<td>5</td>
<td>350</td>
</tr>
<tr>
<td>2-EH-HS</td>
<td>2-EH</td>
<td>2-ethylhexanates (Sm$<em>{0.3}$, Ho$</em>{0.7}$)Ba$_2$Cu$_3$O$_y$</td>
<td>450</td>
<td>860</td>
<td>5</td>
<td>350</td>
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</table>

Surface morphology of the films was observed by scanning electron microscope (SEM), and crystallization of films was observed by x-ray diffraction (XRD) using 0-2θ method with Cu-K$_{α1}$ radiation. Temperature dependence of magnetic susceptibility at 0.001 T in ZFC-FC conditions was measured by superconducting quantum interference device (SQUID) magnetometer. Applied field dependence of magnetization was also measured by SQUID magnetometer. Temperature dependence of critical current density ($J_c$) was estimated from the magnetization using the Bean critical state model. [11]

3. Result

Figures 1 (a)-(d) show SEM images of the surface for the CS-Gd, the 2-EH-Gd, the 2-EH-GP and the 2-EH-HS films, respectively. For 2-EH-Gd, 2-EH-GP, 2-EH-HS, small pores were observed on the surfaces. In contrast, the surface of CS-Gd seems relatively smooth, and there are little pores on the surface. However, the round micron-size precipitates exist on the surface of CS-Gd. The composition analysis using energy dispersive x-ray spectroscopy (EDS) indicated that the precipitates contained Ba and Cu ions. [10]
Fig. 1 SEM images for (a) the surface of CS-Gd film, (b) the surface of 2-EH-Gd film, (c) the surface of 2-EH-GP film, (d) the surface of 2-EH-HS film, respectively.

Figure 2 (a) shows XRD pattern for all films. The intensity is normalized by (006) peak amplitude. Peaks of c-axis oriented phase are remarkably observed for all films. In contrast, peak of a/b-axis oriented phase is not observed, because higher temperature process inhibits a/b-axis oriented phase growth [12]. Thus high-quality crystallization was achieved for all films. Figure 2 (b) shows an enlargement of (006) peaks. The (006) peak of CS-Gd film slightly shifts to lower angle side in comparison with that of other films and the half width is broader than that of others. This suggests that different phases may be introduced into CS-Gd film.

Figure 3 shows the temperature dependence of magnetic susceptibility for all films. The $T_c$'s are estimated to be 84.8, 90.7, 90.0 and 89.1 K for CS-Gd, 2-EH-Gd, 2-EH-GP and 2-EH-HS films,
respectively. The $T_c$ of CS-Gd film is lowest among all films. This is considered to come from the proximity effect due to introduced pinning centers. The magnitude of a magnetic susceptibility at 77 K for each film is corresponding to the magnitude of $J_c$ as shown in figure 4.

![Figure 3](image1.png)  
**Fig.3** Temperature dependence of magnetic susceptibility for all films.

![Figure 4](image2.png)  
**Fig.4** Temperature dependence of $J_c(0)$ for all films.

Figure 4 shows the temperature dependence of $J_c$ at self-field for all films. The CS-Gd film shows the maximum $J_c$ of 30 MA/cm² at 4.2 K. The $J_c$ of other films are 17.8, 7.4, 3.31 MA/cm² at 4.2 K, for 2-EH-HS, 2-EH-GP and 2-EH-Gd films, respectively. In contrast, the 2-EH-HS film shows the maximum $J_c$ of 2.19 MA/cm² at 77K. The $J_c$ of other films are 0.92, 0.88, 0.51 MA/cm² at 77 K for 2-EH-Gd, 2-EH-GP and CS-Gd, respectively. The reason that the $J_c$ of 2-EH-GP showed high value was considered that Pt acted as an effective pinning center. The reason that the $J_c$ of 2-EH-HS showed high value was considered that defects introduced by disorder at the RE site acted as effective pinning center. The $J_c$ of 2-EH-HS is about 2.38 times as large as $J_c$ of 2-EH-Gd at 77K. The $J_c$ of CS-Gd film is about 9.1 times as large as the $J_c$ of 2-EH-Gd at 4.2K. In contrast, the CS-Gd film is about 0.55 times as small as $J_c$ of 2-EH-Gd at 77K. As shown in fig.4, anomalous behaviour of $J_c$ is observed only in CS-Gd.

4. Discussion

In general superconducting films having high $J_c$ at 77 K have also high $J_c$ at low temperatures as 2-EH-HS film derived maximum $J_c$ of 2.19 MA/cm² at 77 K and high $J_c$ of 17.8 MA/cm² at 4.2 K and self-field. On the contrary CS-GdBCO film achieved much higher $J_c$ of 30 MA/cm² at 4.2 K in spite of remaining low $J_c$ of 0.51 MA/cm² at 77 K. An anomalous temperature dependence of $J_c$ was also observed for CS-GdBCO film.
Figure 5 shows the temperature dependence of \( J_c \) at 0.1 T and high temperature range (60-77 K) for all films. It is noteworthy that the slope of the temperature dependence of \( J_c \) changes dramatically at 70.5 K only for CS-Gd film. This suggests the flux pinning mechanism changes at around 70.5 K for the CS-Gd film. It is reported that lower-\( T_c \) regions such as substituted regions or oxygen-deficient regions act as pinning centers in GdBa\(_2\)Cu\(_3\)O\(_y\) films [13]. As shown in figure 1(a), CS-Gd film has Ba- and Cu-rich precipitates in comparison with other 2-EH-films. Thus it is considered that some Ba sites substituted by Gd ions exist in the CS-Gd film as flux pinning sites. This is also supported by observation of low \( T_c \) for CS-Gd films (see figure 3) according to proximity effect of the lower \( T_c \) regions in the superconducting matrix. The elementary pinning force \( f_p \) for very thin superconducting pins in which the spatial variation of the order parameter of superconducting matrix is very small due to the proximity effect [14] can be expressed by sum of potential energy interaction \( f_{pp} \) and kinetic energy interaction \( f_{pk} \):

\[
f_{pp} = 0.479 \pi \frac{d_p^2 \xi}{\mu_0} \left( B_{cp}^2 - B_c^2 \right),
\]

(1)

\[
f_{pk} = 0.296 \pi \frac{d_p}{\mu_0 \xi} \left( B_{cp}^2 \xi_p^2 - B_c^2 \xi^2 \right),
\]

(2)

\[
f_p = f_{pp} + f_{pk}.
\]

(3)

Where \( d_p \) is the pin size, \( \xi, \xi_p \) and \( B_c, B_{cp} \) are the coherence lengths and thermodynamic critical fields of superconducting matrix and superconducting pins, respectively [15]. In this case kinetic energy interaction is dominant pinning energy and generates repulsive pinning force. Above \( T_c \) for lower-\( T_c \) region S-N transition occurs, and thus the lower \( T_c \) region becomes normal conductor with condensation energy interaction. Figure 6 shows the temperature dependence of flux pinning force density \( F_p \) for several kinds of NbTi wires with artificial superconducting pins introduced into NbTi superconductor [15]. The \( F_p \) increases with increasing kinetic energy interaction of each superconducting pin. Here, it is clearly observed that the slope of temperature dependence of \( F_p \) changes at 4.4 K in which S-N transition
occurs for Ta pins. This behaviour is remarkably similar to that for CS-Gd film. This consistency is speculated that lower-$T_c$ regions act as strong pinning centers at low temperatures for the CS-Gd film.

5. Conclusion

We studied the relationship between micro structure and flux pinning properties for several kinds of REBCO films fabricated by a MOD technique using MN and 2-EH solutions. $(\text{Sm}_{0.3}, \text{Ho}_{0.7}) \text{Ba}_2 \text{Cu}_3 \text{O}_y$ film prepared by 2-EH solution achieved the maximum $J_c$ of 2.19 MA/cm$^2$ at 77 K under self-field due to introduction of effective pinning sites. $\text{GdBa}_2\text{Cu}_3\text{O}_y$ film prepared using complex solutions (CS) obtained high $J_c$ of 30 MA/cm$^2$ at 4.2 K in spite of having low $J_c$ of 0.51 MA/cm$^2$ at 77 K. Anomalous temperature dependence of $J_c$ was also observed for CS-GdBa$_2$Cu$_3$O$_y$ film. It suggests that strong pinning centers are induced into CS-GdBa$_2$Cu$_3$O$_y$ film at low temperatures. It is speculated that lower-$T_c$ regions such as substituted regions act as effective pinning centers in the CS-GdBa$_2$Cu$_3$O$_y$ film by comparison analysis with flux pinning for NbTi with different superconducting artificial pins.

References