RCE-DR, a novel process for coated conductor fabrication with high throughput

J.-H. Lee¹, H. Lee¹, J.-W. Lee², S.-M. Choi², S.-I. Yoo² and S.-H. Moon¹,*

¹ SuNAM Co., Ltd., Ansung, Gyunggi-do 456-812, Korea.
² Department of Materials Science & Engineering and Research Institute of Advanced Materials (RIAM), Seoul National University, Seoul, Korea.

E-mail: smoon@isunam.com

Abstract
We report in detail on SuNAM’s reactive co-evaporation by deposition and reaction (RCE-DR) process. We have successfully fabricated high-performance GdBCO Coated Conductor (CC) with high throughput by the RCE-DR process that consists of two steps for the deposition of elemental metal oxides and the conversion of cation oxides into the GdBCO superconducting phase. Constituting metals such as Gd, Ba and Cu were first deposited on LaMnO₃ (LMO)-buffered IBAD-MgO templates at low temperatures and low pressures followed by a high temperature treatment step under high oxygen partial pressure for fast phase-conversion. GdBCO CCs fabricated by RCE-DR showed excellent transport properties such as a critical current of 794 A/cm-width at 77 K in self-field. With the RCE-DR process, we have achieved an overall processing speed of more than 120 m/hr (in terms of a real process linear tape speed equivalent). SuNAM’s RCE-DR technique showed great potential as the highest throughput fabrication process compared to other methods developed previously for the second generation high temperature superconducting wires, meeting the current and future need of industry in terms of price and production speed.

1. Introduction

The second generation high-temperature superconducting (2G HTS) wires, also called CC, have received extensive attention from both academia and industry because of their superior characteristics such as higher current carrying capability and better in-field characteristics compared to the 1st generation wires. However, a full-scale commercialization of REBCO CCs has not been perfected yet in part due to an inherently slow fabrication process that is sub-divided into a series of deposition and heat-treatment steps. Thus, high-throughput process development leading to low fabrication cost is critical to a successful penetration into current and future application markets. Although continuous efforts to fabricate high performance 2G HTS wires have resulted in various methods such as Pulsed Laser Deposition (PLD) [1], Metal Organic Deposition (MOD) [2], Metal Organic Chemical Vapor Deposition (MOCVD) [3] or Reactive Co-Evaporation by Cyclic Deposition and Reaction (RCE-CDR) [4,5], none of them seems to be an economically viable process to meet the needs of markets in the field of electric power, energy, bio-medical, etc. Recently, SuNAM developed a novel RCE-DR process to fabricate high performance GdBCO CCs with extremely high throughput [6]. The RCE-DR is basically a two-step process that consists of fast co-evaporation of precursor films at low temperature under low oxygen pressure (PO₂) and subsequent annealing at high temperature under high PO₂ as shown in Fig. 1. An appropriate feedback algorithm can keep the composition of the superconductor in the desired range, while the deposition rate of each material is monitored with a Quartz Crystal Microbalance (QCM) to adjust the e-beam power. In the RCE-DR process, tapes on which an amorphous precursor layer is first formed at low temperature under low PO₂ by e-beam co-evaporation continuously pass through the high temperature furnace that has two different PO₂ zones in series for the conversion into superconducting phase. The superiority of RCE-DR compared with other techniques lies in the fact that the fabrication of high quality GdBCO CCs is possible with high speed which, in our case, is at least 360 m/hr (4 mm-width equivalent). High deposition rates owing to highly efficient e-beam co-evaporation at low temperatures and low oxygen partial pressures, followed by a fast conversion of the amorphous phase into the superconducting phase at high temperatures and high
oxygen pressures, are the key features of SuNAM’s RCE-DR process. Unlike some other co-evaporation processes such as RCE-CDR or Evaporation using Drum in Dual Chamber (EDDC) requiring multiple cycles of deposition and conversion, SuNAM’s RCE-DR process was designed to form a superconducting layer by a single pass in which the amorphous glassy phase previously deposited by co-evaporation is rapidly converted into the superconducting phase at once. In this paper, we discuss in detail the characteristics of GdBCO CCs fabricated by SuNAM’s RCE-DR process.

2. Experimental

The typical layer structure of GdBCO CCs fabricated for this study is shown in Fig. 2. The GdBCO CCs were fabricated by the RCE-DR process on LaMnO$_3$-buffered IBAD-MgO templates [7]. An amorphous precursor film was deposited first by a RCE system equipped with a single Pierce type e-beam gun which was adjusted to operate in a specific scan pattern to evaporate three different metal sources of Gd, Ba, and Cu simultaneously. The deposition of each metal was monitored by QCM and feedback controlled by a computer system which adjusts the scan pattern and the beam current. The specially designed program controls the deposition rate of each element by adjusting durations in which the e-beam shines on each source and the beam current to get the proper composition of the precursor film. The nominal composition of such formed amorphous film was Gd : Ba : Cu ≈ 1 : 1 : 2.5. Then, the as-deposited amorphous precursor film was transferred to a hot zone of a tube furnace with lower oxygen pressure of ~ 10$^{-5}$ Torr and subsequently moved into higher oxygen pressure zone of ~ 150 mTorr for conversion into the GdBCO phase. The transport properties of the GdBCO CCs fabricated by various RCE conditions were measured and compared to find out an optimum composition of Gd$_2$O$_3$, BaO, and CuO$_2$ phases in the precursor for higher values of critical currents. The effect of oxygen pressure on the crystallinity of the GdBCO formed during annealing process in the furnace was also observed for fine-tuning of phase-conversion conditions. The phase and texture of GdBCO CCs were characterized by X-ray diffraction (XRD) using CuKα radiation and energy dispersive spectroscopy (EDS). The c-axis orientation of GdBCO CCs were studied by collecting rocking curve data for the GdBCO (005) peak. Also, for investigating in-plane orientations of the GdBCO CCs, ϕ-scan data for the GdBCO (103) peak were collected. Cross-sectional analysis of GdBCO CCs was done by a transmission electron microscope (TEM). R–T and I–V characteristics were evaluated by a standard four-point probing method.

3. Results and Discussion

Fig. 3 shows the R-T (a) and XRD (b, c, d) characteristics of the GdBCO CCs fabricated by RCE-DR for this study. As shown in Fig. 3(a), the critical temperature ($T_C$) of GdBCO CCs fabricated in this study is 94.5 K and the highest value of critical current ($I_C$) is 794 A/cm-width at 77 K, self-field. XRD θ–2θ scan patterns shown in Fig. 3(b) confirm that GdBCO fabricated by RCE-DR has a strong c-axis oriented crystal structure. ϕ-scans shows 4 peaks with 90 degrees separation, implying that GdBCO CCs are biaxially textured. The full-width at half-maximum (FWHM) of ω-scan and ϕ-scan results shown in Fig. 3(c) and 3(d) are 2.84° and 4.28°, respectively, showing good crystallinity, both for in-plane and out of plane directions.

In this study, the effect of PO$_2$ on the crystallinity and texture of GdBCO films was thoroughly investigated. To avoid the effect of other processing parameters, the GdBCO precursor samples used for the characterizations were carefully chosen in the same batch. As shown in Fig. 4(a), it is clearly seen that GdBCO could not be formed effectively at low oxygen pressure, while strongly c-axis oriented GdBCO was obtainable at higher oxygen pressure.

GdBCO films with poor in-plane texture, however, were obtained at very high oxygen pressure conditions as represented in Fig. 4(b). It is, therefore, obvious that an optimum oxygen pressure (~100 mTorr) to create excellent crystallinity of GdBCO film exists. As shown in Fig. 4(a) and (b), no discernible peaks are detected from the XRD pattern.
the sample fabricated at lower oxygen pressures (50 mTorr), while noticeable peak-broadenings are observed from the sample fabricated at very high oxygen pressure. Considering the stability phase diagram of GdBCO, a low oxygen pressure in the GdBCO region matches the low temperature as known from the temperature of the GdBCO-phase-boundary [8] conversion temperature of GdBCO for the formation of GdBCO from the Gd$_2$O$_3$ + L state. Thus a highly biaxially textured GdBCO film was able to be formed by a small driving force that initiated nucleation of GdBCO.

For fast conversion of GdBCO in the RCE-DR process, the composition of precursor films is crucial to the growth of GdBCO film and its superconducting property. In this study, the effect of composition of GdBCO films on $I_C$
was also studied. To consider the composition as a variable parameter, other experimental conditions such as temperature, oxygen pressure and moving speed of substrate during the deposition were fixed as 870 °C, 150 mTorr, and 2 m/min, respectively. Since the compositions analyzed by EDS are heavily affected by surface condition of films, inductively coupled plasma (ICP) analysis was done to confirm the composition of GdBCO films. Fig. 5(a) shows the relationship between the specific combination of composition and its resulting $I_C$ of GdBCO films on the $\frac{1}{2}$ Gd$_2$O$_3$-BaO-CuO$_z$ ternary phase diagram. It can be seen that all samples analyzed in this study have the Ba-deficient (Ba < 33.3%) and Cu-rich (Cu > 50%) composition compared to stoichiometric GdBCO. From the enlarged section near stoichiometric GdBCO in Fig. 5(b), the nominal composition ratio of metal sources to get the highest $I_C$ of GdBCO turns out to be 1 : 1 : 2.5 (Gd : Ba : Cu). It should be noted that the Gd content (~22.2%) is higher than that of stoichiometric GdBCO (~16.7%). Since the RCE-DR is essentially melt-grown process by the peritectic recombination of Gd$_2$O$_3$ + L, a sufficient supersaturation of Gd$_2$O$_3$ in the ternary liquid phase is necessary for the proper growth of the GdBCO films [9]. It is similar to the melt-growth of GdBCO bulk, in which the composition of GdBCO + excess Gd$_{211}$ is used. However, the composition to get the high $I_C$ is not fixed but variable depending on the other processing parameters such as temperature and oxygen pressures. Therefore, the relation between the composition and other processing parameters to obtain the highest $I_C$ from GdBCO film should be further investigated.

The GdBCO CCs fabricated by RCE-DR process shows excellent transport properties. Fig. 6 shows the measured $I_C$ values of GdBCO CCs fabricated by RCE-DR process in this study. The $I_C$ measurements were done in a specifically designed system to evaluate the transport properties of GdBCO CCs [10]. The average of measured $I_C$ values for this GdBCO sample is 794 A/cm-width at 77 K in self-field with the standard deviation of 17 A and a coefficient of variation (COV) of 2.1%. The COV represents a uniformity of the measured $I_C$ values, as computed by following formulas:

\[
COV_{\text{min-max}} = \frac{|I_C^{\text{max}} - I_C^{\text{min}}|}{\bar{X}} \times 100(\%) \quad (1)
\]

\[
COV = \frac{\sigma}{\bar{X}} \times 100(\%) \quad (2)
\]

where $\bar{X}$ and $\sigma$ denote the average value and standard deviation of the current.

TEM analysis was done on GdBCO samples to confirm the proper depositions of individual layer as well as the dispersion of Gd$_2$O$_3$ second phases [11]. Cross-sectional TEM image in Fig. 7(a) shows uniformly formed multilayers of typical GdBCO CCs fabricated by RCE-DR process. The Gd$_2$O$_3$ second phases are uniformly dispersed throughout the cross-section of GdBCO layer as shown in Fig. 7(b).

Figure 5(a) $\frac{1}{2}$ Gd$_2$O$_3$-BaO-CuO$_z$ ternary phase diagram. $I_C$ distribution depending on the film composition is presented by the color of the composition point in the phase diagram.

(b) $\frac{1}{2}$ Gd$_2$O$_3$-BaO-CuO$_2$ ternary phase diagram (magnified). $I_C$ distribution depending on the film composition is presented by color of the composition point in the phase diagram. Nominal composition of Gd : Ba : Cu ≈ 1 : 1 : 2.5 for high- $I_C$ GdBCO is designated by the dashed circle (orange color).

Figure 6. The critical current characteristics of GdBCO CCs fabricated by RCE-DR.
4. Conclusion

We successfully fabricated GdBCO CCs on LMO-buffered IBAD-MgO templates by the RCE-DR process. The critical temperature and the critical current measured for GdBCO CCs fabricated by RCE-DR process are 94.5 K and 794 A/cm-width at 77 K in self-field, respectively. TEM analysis shows the uniformly deposited multi-layer structure of GdBCO CCs as well as the uniformly dispersed Gd$_2$O$_3$ second phases. In this study, we were able to achieve not only high performance GdBCO CCs but also high throughput in the fabrication process, which is a prime advantage of the RCE-DR process. To further raise the throughput of RCE-DR process, we have been working on plans to increase the width of GdBCO CCs to 120 mm.

It was also confirmed that the composition of Gd$_2$O$_3$-BaO-CuO$_2$ phases is closely related to the resulting $I_c$ performance of GdBCO CCs. It is assumed that the extra Gd$_2$O$_3$ phases are required for the proper formation of GdBCO film during the RCE-DR process. Although it was proved that the excellent quality and high throughput can be attained from GdBCO CCs fabricated by RCE-DR process, in-field pinning characteristics remain to be improved further in the future.

Acknowledgment

The authors express sincere thanks to Robert Hammond of Stanford University, Vladimir Matias of iBeam Materials, H. S. Ha and S. Oh in Korea Electro-technology Research Institute (KERI) for invaluable discussion.

This work was supported by the Power Generation & Electricity Delivery of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy (No. 20131010501800)

References