Chemical Modification of Precursor Solution for Long Length YBCO Coated Conductor Fabrication

Jaimoo Yoo, Young-Kuk Kim, Kookchae Chung, Jaewoong Ko,
Gye-Won Hong\textsuperscript{a}, Hee-Gyoun Lee\textsuperscript{a}, Jin-Heung Kim\textsuperscript{b},
Hyungsik Chung\textsuperscript{a}, X. L. Wang\textsuperscript{d}, S. X. Dou\textsuperscript{d}

Korea Institute of Machinery and Materials (KIMM), Republic of Korea
\textsuperscript{a}Korea Polytechnic University, Republic of Korea
\textsuperscript{b}Ewha Women’s University, Republic of Korea
\textsuperscript{c}Ajou University, Republic of Korea
\textsuperscript{d}University of Wollongong, Australia

Abstract

Long length MOD processing of YBCO conductor requires high performance precursor solution without degradation during the process. In this study, effect of chemical modification of precursor solution on MOD processing was investigated to meet the requirement. Highly stable YBCO precursor solution was synthesized with PVP (polyvinylpyrrolidone) and crack-free thick precursor film was successfully fabricated. However, annealed YBCO film shows porous microstructures originated from large HF gas generation from thick films and residual carbon from additives. Reduction of fluorine content is required to densify microstructures. In order to reduce fluorine content, F-free Cu-precursor solution was synthesized. YBCO film with $J_c=0.8\text{MA/cm}^2$ was grown on buffered RABiTS tape. Annealed YBCO film still contains pores and further reduction of pores is required to improve critical current ($I_c$).

1. Introduction

The YBa$_2$Cu$_3$O$_{7-x}$ (YBCO)-based coated conductor (CC) is promising high temperature superconducting (HTSC) wire architectures for electrical devices [1]. Many efforts are in progress to develop long HTSC wire with high current carrying capacity by coated conductor architecture [1-3]. Among them, metal-organic deposition using trifluoroacetates (MOD-TFA) is attracting more interest because of its potential for scale-up and cost-effectiveness. MOD-TFA is chemical solution deposition process which is intrinsically non-vacuum approach and YBCO thin films with relatively high $J_c$ (>1MA/cm$^2$) can be routinely fabricated by this process [4-7].

In order to obtain YBCO CC with high critical current, several requirements such as dense microstructure, clean grain boundary, fine precipitate for flux pinning, increasing thickness per coating, etc. should be satisfied. In MOD-TFA process, one of the most important issue in the fabrication of YBCO coated conductor with high $I_c$ is the synthesis of MOD precursor solution. In particular, long length processing of coated conductor requires stable precursor solution.
In this study, effect of chemical modification of precursor solution on MOD processing was investigated to meet the requirement for high Ic. In particular, the effect of chemical modification of precursor solution on microstructure and thickness of YBCO or precursor film was checked. Chemical modification of precursor solution was performed by adding organic additives or substituting F-free Cu precursor for Cu-trifluoroacetate.

2. Effect of PVP (Polyvinylpyrrolidone) addition

In chemical solution processing of thick ceramic films, organic additives such as 1, 3-propanediol, ethylene glycol etc. are employed to improve stability of precursor solution and fabricate crack free thick films [8,9]. V. L. Tu et al. deposited 1μm-thick & crack-free Pb(Zr,Ti)O₃ (PZT) films using chemical solution deposition with 1,3-propanediol containing precursor solution. Recently, H. Kozuka et al., fabricated 2μm-thick PZT films without any crack by PVP-assisted Sol-gel process. It is known that addition of PVP in precursor solution improve stability of precursor solution by inhibiting condensation reaction and increase critical thickness for crack generation [10]. P. Clem et al. shows that PVP can reduce film stress and increase the thickness of YBCO film prepared by PVP-assisted SANDEATM solution [11].

In this study, in order to improve stability and thickness of YBCO film, PVP was incorporated into our YBCO oxide-based precursor solution. Fig. 1 shows surface of the precursor film after calcination using PVP-assisted YBCO precursor solution. No crack was detected and uniform surface was shown.

![Fig. 1. Surface of as-calcined precursor film. (a) OM, (b) SEM](image)

By controlling concentration of PVP, thickness of crack-free precursor film was linearly increases to 2μm (Fig. 2(a)). This means PVP act as stress releasing agent and improve critical thickness of precursor films. In addition, time-dependent variation of solution viscosity is negligible, which indicates excellent stability of precursor solution with PVP (Fig. 2(b)).

![Fig. 2. (a) Thickness of precursor films after calcination as a function of concentration of PVP, (b) stability of precursor solution with PVP](image)
1.5μm-thick precursor film was converted to YBCO films after annealing. The thickness of YBCO film was about 0.7μm (Fig. 3). However, surface and cross-section of annealing YBCO film shows a large amount of pores exists and size of pores are very large. As a result of this, the measured Ic value of this sample is only 2A. The origin of these large pores is attributed to large HF generation from thick precursor film during the annealing process and possible residual carbon from additives [12]. This shows that a new solution with low HF content is required to inhibit pore formation.

Fig. 3. Microstructure of converted YBCO film after annealing. (a) surface, (b) cross-section

3. F-free Cu precursor solution
F-free Cu precursor solution was synthesized by dissolving F-free Cu precursor into methanol with Yttrium and Barium trifluoroacetate. Since the total content of Fluorine in the precursor solution is half of conventional MOD-TFA precursor solution, much faster calcinations profile compared with that of conventional MOD-TFA process was applied. Only 2~3 hours are required to finish calcinations process. In this study, buffered RABiTS tape was used as substrate for coating. Fig. 4 presents as-calcined surface of the precursor film which shows crack-free 1.7μm-thick film. Thickness of precursor film is beyond the range of conventional MOD-TFA solution (t~1μm). This can be attributed to much lower HF gas generation during calcinations process compared with conventional MOD-TFA process.

Fig. 4. Surface of calcined precursor film using F-free Cu precursor solution. (a) OM, (b) SEM

The calcined precursor film was converted to YBCO film after annealing process in Ar/O2 atmosphere. DC 4-probe measurement shows that critical current of YBCO film was about 0.8MA/cm^2. Microstructural investigation indicates that pores still exist and further removal of pores is required to improve critical current of the YBCO film. It is known that low pressure annealing will improve growth rate of YBCO film and suppress HF gas build-up during the conversion process [13]. In order to improve microstructure and critical current of YBCO film, low pressure annealing will be applied to convert precursor films to YBCO films.
4. Summary
In summary, PVP-containing precursor solution was synthesized and YBCO film shows porous microstructures originated from large HF gas generation from thick films and residual carbon from additives. Reduction of fluorine content is required to improve microstructures.

In order to reduce fluorine content, F-free Cu-precursor solution was synthesized. A crack-free 1.7mm-thick precursor film was fabricated through fast calcinations process. Converted YBCO film shows critical current of 0.8MA/cm$^2$. Microstructure of YBCO film still contains pores and further reduction of pores is required for higher Ic.

Low pressure annealing will be applied to achieve high Ic through fast growth rate and inhibition of HF gas build-up.

Acknowledgement
This research was supported by a grant from the Center for Applied Superconductivity Technology of the 21st century Frontier R&D Program funded by the Ministry of Science and Technology, Republic of Korea.

References
[1] R. J. Soulen, Jr., D. –W. Yuan, T. L. Francavilla, IEEE trans. Appl. Supercon., 11 (2001), p.2995.
[2] K. Hasegawa, N. Yoshida, K. Fujino, H. Mukai, K. Hayashi, K. Sato, Y. Sato, S. Honjo, T. Ohkuma, H. Ishii, T. Tara, Advances in Superconductivity IX, eds. S. Nakajima, and M. Murakami, Springer-Verlag, Tokyo (1996)
[3] J. Knauf, R. Semerad, W. Prusseit, B. DeBoer, J. Eickemeyer, IEEE Trans. on Appl. Supercon., 11 (2001), p.2885.
[4] S. Miura, K. Hashimoto, F. Wang, Y. Enomoto, T. Morishita, Physic C, 278 (1997), p.201.
[5] S. Sathyamurthy and K. Salama, IEEE Trans. on Appl. Supercon., 11 (2001), p.2935.
[6] D. T. Verebelyi, U. Schoop, C. Thieme, X. Li, W. Zhang, T. Kodenkandath, A. P. Malozemoff, N. Nguyen, E. Siegal, D. Buczek, Supercod. Sci. and Tech. 16 (2003), p.L19.
[7] J. T. Dawley, P. G. Clem, M. P. Siegal, D. L. Overmyer, J. Mater. Res., 16 (2001), p.13.
[8] Y.L. Tu et al., J. Mater. Res. 11, 2566 (1996)
[9] K. Maki et al., J. Am. Ceram. Soc. 83, 1914(2000)
[10] H. Kozuka et al., J. Am. Ceram. Soc., 85, 2696 (2002)
[11] P. Clem et al., CCA2004, Oiso, Japan (2004)
[12] T. Araki, I. Hirabayashi, Supercond. Sci. Technol. 16, R71 (2003)
[13] Ryo Teranishi, Tetsuji Honjo, Yoshitaka Tokunaga, Hiroshi Fuji, Junko Matsuda, Teruo Izumi, Akimasa Yajima and Yuh Shiohara, Physica C 412-414, 920 (2004)