Effect of interim annealing on mechanical strength of TFA-MOD derived YBCO coated conductors

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Abstract

TFA-MOD derived YBCO tapes are expected for many applications due to cost-efficiency. In some applications, uniformity and mechanical strength are required for tapes. A 205 m-long YBCO tape was fabricated with high and uniform $I_c$ performance throughout the tape by adopting the interim annealing before the conversion process. The effect of the interim annealing on the crystal growth mechanism of YBCO has been studied focusing on the relationship between the interim annealing conditions and delamination, in this work. Delamination strength was evaluated in the samples prepared with and without interim annealing by the stud pull method. Measurements were carried out on 50 different points for each sample and the results were analyzed statistically. The difference between the two samples was remarkably seen in the delamination strength below 60 MPa. The conventionally annealed sample had more points with low delamination strength below 60 MPa than the interim annealed one. The cross sectional images of both samples observed by SEM showed that there were few pores within the interim annealed superconducting layer, although conventional superconducting layer had many pores. These results suggest that the pores within YBCO layer might be origins to be propagated for delamination at low strength.

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1. Introduction

RE$_x$Ba$_2$Cu$_3$O$_y$ (REBCO, RE: Y and rare earth) coated conductors (CCs) are expected to be promising candidates as high performance superconducting wires, therefore, R&D of CC has been actively carried out all over the world. In order to realize various applications, high critical current ($I_c$), cost reduction and high mechanical strength are required. The trifluoroacetate metal-organic deposition (TFA-MOD) process is known as a cost effective process to yield CCs with high critical current density ($J_c$).

The CCs using Hastelloy™ as substrates have high mechanical strength in tensile stress along tape surface. However, these are easily delaminated by tensile stress perpendicular to tape surface. Multifilamentation is one of the effective approaches to reduce AC loss and required for many applications, however, YBCO CCs fabricated by conventional TFA-MOD process often delaminate into two parts by the multifilamentation processing.

Recently, we modified the TFA-MOD process by inserting the interim annealing between calcination and conversion. By adopting the interim annealing, we successfully fabricated a 205 m-long YBCO CC at high throughput (15 m/h) with high and uniform $I_c$ performance: $I_c$ (min.) = 372 A/cm-W at 77 K, s.f., standard deviation = 15.2 A (3.7 %) along the longitudinal direction[1]. A 50 m long YBCO CC with 5 mm width fabricated using the interim annealing was successfully scribed into five filaments without delamination through the whole length [2]. In this work, the effect of interim annealing on delamination strength was investigated and the mechanism of delamination was discussed from the viewpoint of YBCO crystal growth mechanism.

2. Experimental

The starting solution for coating was prepared by dissolving Y-TFA, Ba-TFA, and Cu-2-ethylhexanoate into an organic solvent to be the atomic ratio of Y:Ba:Cu = 1:1.5:3 [3]. The starting solution was dip-coated on buffered tapes of CeO$_2$ ($\Delta$ = 3.5°)/LaMnO$_3$/IBAD-MgO/Gd$_2$Zr$_2$O$_7$/Hastelloy™ C276 using a multi-turn RTR system. The coated tapes were calcined to form precursor films at 500°C in a humid oxygen atmosphere. The coating/calcination decomposing process was repeated to obtain a film thickness of 1.5 $\mu$m. Two 0.5m long precursor films were prepared for the following heat treatment. One was interim annealed and another was not. The conditions of the interim annealing were 575°C for 3 hours in dry argon. The precursor tapes with and without the interim annealing were heated up to 760°C ($T_{max}$) in humid N$_2$ + O$_2$ ($P_{O2}$ = 0.4 vol%) atmosphere to crystallize YBCO using a RTR system. Experimental conditions of the crystallization process were as follow; total pressure, gas flow rate, water vapor partial pressure, and tape travelling rate were 40–45 Torr, 140 L/min, 14 Torr, and 15 m/h, respectively. The crystallinity of the films was evaluated by X-ray diffraction (XRD). The pores and thickness were analyzed by the SEM observation. The converted films were cut into small pieces (1 cm × 1 cm) for delamination strength measurement; a stud pin with the diameter of 2.7 mm was bonded to the CCs by epoxy resin and pull down along the vertical direction against the surface by using a Romulus™ system.

3. Results and Discussion

Delamination strength was measured on 50 different points for each sample and the results were analyzed statistically (see Fig. 1). The conventionally annealed sample contained more points below 60 MPa than the interim annealed one did.

Figs. 2(a) and (b) are the cross-section SEM images of conventional and interim annealed samples. There were three differences observed between these samples: (1) number and size of the pores (2) shape of the pores (3) thickness of YBCO layer. There were many pores with variety of the size in the case of conventional sample (Fig. 2(a)). In contrast, a few and almost small pores were observed in the case of the interim annealed sample (Fig. 2(b)). There were various shaped pores with a distorted and circular observed in the conventional sample though nearly circular pores in the interim annealed sample. YBCO thickness conventionally and interim annealed was 1.86 $\mu$m and 1.59 $\mu$m, respectively. This means that the film became about 15% denser by adopting the interim annealing.
Considering the microstructures obtained from cross-section SEM images, it was suggested that the pores in YBCO layer might be origins to be propagated for delamination at low strength. The low strength points were suppressed by adopting the interim annealing, but still remained (26 %), which corresponded to the pores distribution. To realize TFA-MOD CCs with high delamination strength for wider applications, “pore-free film” is required.

In order to realize the pore-free film, the mechanism of pore generation should be understood. Two mechanisms are considered about the formation of the pores. One is the reaction in solid state after an epitaxial growth of REBCO layer, which was firstly reported by J.S. Matsuda et al. They explained the mechanism was the volume reduction about 30% \[4\] due to YBCO formation with the following reaction:

\[
\frac{1}{2} Y_2Cu_2O_5 + 2BaF_2 + 2CuO + 2H_2O \rightarrow YBa_2Cu_3O_{(6.5-2x)} + 4HF + \frac{x}{4} O_2
\]

(*)

In this mechanism, unreacted phases are firstly entrapped into YBCO during epitaxial growth in a layer-by-layer manner. They react with each other to form YBCO in solid state reaction with accompanied by the volume reduction, forming the pores within YBCO. As the countermeasure to this mechanism, complete reaction during YBCO epitaxial growth should be realized. We assume that optimization of the interim annealing is effective to control growth rate of YBCO and size of precursor phase particles, which could be a solution.

Inhomogeneous film shrinkage is another mechanism of pore formation. The precursor films are shrank during the crystallization heat-treatment. In this process, there are several inhomogeneous conditions which relate shrinkage, e.g. fluorine contents, metal composition and temperature uniformity in precursor films. As temperature increase, liquid phase is generated at certain points and local gas release is suppressed underneath the liquid and then the residual gas might become pores. The approach for this origin of pores is to improve homogeneity in

![Fig. 2. Cross-section SEM image (a) without interim annealing and (b) with interim annealing](image)
precursor film. Yoshizumi et al. and W Wong-Ng et al. have reported the possibility that the liquid phase exists in this system in the range of temperature above 550°C [5, 6]. As temperature increase, fluoride reacts with H2O to form oxide and HF gas. In the range of temperature from 500 to 600°C, some amount of melt is generated and the precursor film is shrunk. The amount of melt is decided by fluorine content within the precursor film, and atmosphere. The fluorine content could be controlled by the conditions of the interim annealing, especially It was suggested that temperature and water vapor partial pressure suppressing the excess amount of melt could be effective to eliminate pores.

4. Conclusion

We have investigated the relationship between the interim annealing which enabled to fabricate high \( J_c \) and uniform films at high production rate by TFA-MOD process and the delamination strength evaluated by stud-pull down method. According to the results of delamination strength measurement and microstructure analysis, the outline of histogram was different; the number of points with delamination strength below 60 MPa was reduced by the interim annealing. However, the weak proportion of the weak points was still 26 % the interim annealing. In order to eliminate pores to improve the delamination strength, the mechanism and countermeasure of the pore generation were discussed. There are two possibilities of the mechanism for pore generation; the volume reduction in the solid state reaction and the inhomogeneous reaction in the crystallization heat-treatment. For both mechanisms, the optimization of the interim annealing is considered to be effective to suppress pores.

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References