Crystal growth process of Y123 film fabricated by modified TFA-MOD process

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Abstract. Modified metal-organic deposition (MOD) process using precursor solution of trifluoroacetates (TFA) for Y and Ba and F-free salt for Cu is one of the most promising low cost non-vacuum methods to fabricate the coated conductor of YBa$_2$Cu$_3$O$_{7-X}$ (Y123) film with high critical current density. Since Y123 phase grows in the precursor film by the release of HF with supplying H$_2$O, liquid/gas evolution affects the growth process, microstructure and properties of Y123 film. However, details of the growth mechanism of Y123 crystals are still unknown. To clarify the growth mechanism of Y123 film, the growth process of Y123 crystal was studied by the experimental method and the numerical method (FDM analysis). The quenching experiments during the growth of Y123 crystals on LaAlO$_3$ (LAO) and/or CeO$_2$/LAO substrates revealed the microstructures of growing Y123 crystals through TEM observations. The growth model for Y123 crystals in YBCO film with some process-controlling parameters was obtained on the basis of the experimental results. The growth processes of faceted Y123 crystals with various crystal orientations were simulated by the two-dimensional numerical method using c-axis and a-axis growth rate functions, and the effects of initial distributions of nucleated crystals and particles were discussed.

1. Introduction
Metal organic deposition process using trifluoroacetates (TFA-MOD process) is one of the most promising methods to fabricate high-Jc coated conductors [1-8]. However, there are still some problems such as low-Jc in the thick films [6, 8], which has worse Y123-crystal alignment and/or micro cracks. Y123 phase grows in the precursor film with CuO, Y$_2$Cu$_2$O$_5$ and BaF$_2$ by the release of HF with supplying H$_2$O [9], and so liquid/gas evolution affects the growth process, microstructure and properties of Y123 film. However, details of Y123-crystal growth process are still unknown. In this study, to clarify the growth process and mechanism of Y123 crystals, both experimental and analytical methods were introduced. YBCO films on LaAlO$_3$ (LAO) substrate were quenched during crystallization in the firing process and observed the structures in the cross-sectional area by TEM. Further, two-dimensional numerical simulation of 123-crystal growth in the YBCO film was performed to reveal the growth process.
2. Experimental

We used the modified TFA solution developed by SRL: Superconductivity Research Laboratory. The solution was composed of F-free salt of Cu and TFA salts of Y and Ba with the cation ratio of Y:Ba:Cu = 1:2:3. It was coated on LAO or CeO₂/LAO substrate by spin coating at 4000rpm for 2 min. Then, the gel film was calcined (673K-773K) in moist O₂ atmosphere, and fired (1023K-1033K) using a forming gas (Ar-0.1%O₂-10%H₂O). In the firing process, Y123 grains with c-axis (or a-axis) orientation start to grow epitaxially on LAO or CeO₂/LAO substrate. In order to clarify the growth process of the Y123 crystals in the films by TFA-MOD process, we get the quenched samples during the firing under various conditions, and observed the microstructures of the quenched samples by transmission electron microscopy (TEM).

3. Numerical simulation method

Numerical simulation method is given as follows. This simulation model is shown schematically in Figure 1, which was obtained by modifying the faceted growth model for numerical simulation mentioned in our published papers [14-18, 20].

(1) Elements for FDM analysis to simulate faceted Y123 crystal growth from the liquid (or amorphous) + oxide (or fluoride) particles are selected (element size: ΔX × ΔX (μm²), numbers: nx and ny).

(2) Particles (Y₃Cu₄O₉, CuO, BaF₂ etc.) [9] in the precursor film during the firing are assumed to compose a composite- particles (Y₂BaCu₄OFₓ) in the liquid of Ba₃Cu₄O₉(Y, F), and the initial distribution of the composite particles is given by the following log-normal distribution:

\[ f(r) = \frac{1}{\sqrt{2\pi}\ln\sigma} \exp\left(\frac{-\ln^2(r) - \ln^2(r_m)}{2\ln^2(\sigma)}\right) \]

where, \( f(r) \) initial fraction of composite particles in the precursor, \( r \): radius of particle, \( \ln(r_m) \): arithmetic mean of \( \ln(r) \), \( \ln(\sigma) \): standard deviation of \( \ln(r) \).

(3) Time step is given by: \( \Delta t = \Delta x^2/D \), where, \( D \): diffusion coefficient in the liquid, \( \Delta x \): size of element.

(4) Nucleated Y123-crystals with different crystal orientations are given in some elements by using random numbers.

(5) Growth rate \( V_c(I,J) \) of c-plane (:c-axis growth rate) and \( V_a(I,J) \) of a-plane (:a-axis growth rate) are assumed to be given by the following functions of interface angle(\(\xi\)) with the facet plane (figure 2) [14-18],

\[ V_c = a_c \frac{(X_{123})^{1/2}}{\eta(T)} F(\Delta C) / \eta(T) \]

\[ V_a = a_a \frac{(X_{123})^{1/2}}{\eta(T)} F(\Delta C) / \eta(T) \]

where, \( a_c \) and \( a_a \) are variables: \( a_c = a_{c0} \cdot [(\tan \xi/\beta) \cdot (\tan \beta/\tan \xi) \cdot \{1/\cos(\pi/4) - 1\} + 1] \), \( a_a = a_{a0} \cdot [(\tan \xi/\beta) \cdot (\tan \beta/\tan \xi) \cdot \{1/\cos(\pi/4) - 1\} + 1] \), \( a_{c0} \): constant, and \( a_{a0} = 10^{x} \cdot a_{c0} \) is assumed from the observed data (figure .1), \( \beta = 0.8 \), \( \xi \): angle between the facet and the interface plane, and \( \eta(T) \) (Pa · s): viscosity of the liquid in the precursor: \( \eta(T) = \eta_0 \cdot \exp(E_p/(T - T_0)) \). Vogel-Fulcher Eq., \( A_0 \), \( E_p \) and \( T_0 \) are constants (\( A_0 = 1.0 \times 10^6 \), \( E_p = 6000 \), \( T_0 = 640 \)), and \( h \): tortuous factor in a porous media. \( F(\Delta C) \) is a function of supersaturation (\( \Delta C \)) at the interface: a function of exp(-
B/ΔC) for two dimensional nucleation growth mode, or a function of (ΔC)² for screw growth mode, and a function of ΔC for the most simple model. If the liquid concentration at the interface element changed over an assumed limit, the liquid is trapped in the Y123 crystal.

(6) Increase in fraction of solid (Δfs) and fraction of solid(fs) in the interface element are given by:
\[Δfs = Vk \times Δt \times ΔL\] and \[fs = fsb + Δfs\], where \(ΔL\) is the interface length in the element.

(7) Concentrations of liquid for interface element and for bulk element are calculated by the following equations.

Concentration of liquid \(C_L(I,J)\) for interface element is:
\[C_L(I,J) = C_{in}(I,J) + [Δf_{123}(I,J)Δx^2(C_{in}(I,J) - C_{123}) + Δf_{i}(I,J)Δx^2(C_{i} - C_{in}(I,J))] \frac{Δt}{C_{123}(I,J) - C_{i}} + Δt \cdot D \]
\[\times \left[\left(C_{123}(I,J) - C_{in}(I,J)\right) f_{123} + \left(C_{in}(I,J) - C_{123}(I,J)\right) f_{i} + \left(C_{i}(I,J) - C_{in}(I,J)\right) f_{in}\right]\] \(\cdot \left(1 - fs(I,J)\right) Δx^2\)  

(4)

Concentration of liquid \(C_L(I,J)\) for bulk element is:
\[C_L(I,J) = C_{in}(I,J) + [Δt \cdot D \times \left[\left(C_{123}(I,J) - C_{in}(I,J)\right) f_{123} + \left(C_{in}(I,J) - C_{123}(I,J)\right) f_{i} + \left(C_{i}(I,J) - C_{in}(I,J)\right) f_{in}\right]\] \(\cdot \left(1 - fs(I,J)\right) Δx^2\)  

(5)

where, \(f_{123} = \sqrt{f_{in}(I,J)f_{i}(I,J)}\) and \(f_{i} = \sqrt{f_{in}(I,J)f_{123}(I,J)}\).

Further, it is assumed that this system is quasi-equilibrium state and the liquid in the bulk element is assumed to be in equilibrium with the dispersed particles. So, we calculate the melting of particles in the liquid to change \(C_L(I,J)\) for the equilibrium value with particles.

(9) If interface goes partially to the next element, new interface element and new fs are defined.

(10) Calculated results were saved at selected time, and calculation is repeated after Δt until the end of calculation.

### 4. Results and discussion

#### 4.1. Microstructures observed in the firing process

Figure 3 shows TEM image of cross-sectional area of Y123 film quenched during the firing process Figure 3(a) and (b) are images of Y:Ba:Cu=1:2:3 samples, and figure 3(c) is the image of Y:Ba:Cu=1:1.5:3 sample. Y123 crystals with different orientations are observed in these figures. Some c-axis oriented crystals, which were confirmed by selected area diffraction patterns, are growing on the LAO substrate. Also some a-axis crystals are
observed in the films. The bright region is un-reacted region which was composed of liquid (amorphous) and precipitates ($Y_2Cu_3O_7$, BaF$_2$, CuO etc) [9], [11], [12]. Growth rates ($V_c$ and $V_a$) of c-axis and a-axis orientations can be estimated from the figure, and $V_a$ is larger than $V_c$ ($V_a \geq 10V_c$). In the previous paper [10], we observed the surface changes of the film during firing process (heating to 1048K) by the in-situ observation method, and clarified the generation of liquid phase (and gas) evolution during the firing. From the above observed results, TTT (Time-Temperature Transformation) and CHT (Continues Heating Transformation) diagrams for Y123-cystal growth process were derived and are shown schematically in figure 4. Solid lines show TTT diagram and broken lines show CHT diagram. The position (1) on the line of firing path in the figure corresponds to the initial stage, where mainly c-axis (and sometimes a-axis) grains start to grow on the substrate. Positions (2) and (3) are middle stages of firing, where c-axis and a-axis grains are growing into the un-reacted region and some new grains start to nucleate and grow. The position (4) is final stage of firing.

4.2. Simulated results of faceted 123 crystal growth

Simulated results of growth process of faceted Y123 crystals growing from mixed region of liquid and composite particles (oxides and fluorides) are shown in figure 5. Growing Y123 crystals with c- and a-axed orientations are
well simulated, and their shapes show in good agreement with the experimental results of figure 3. Many c-axis crystals nucleated and are growing from the surface of the substrate(a), and they met each other at the early stage and have meandered and clear interfaces without incorporated liquid (Ba-Cu rich phase)((b)-(d)). The films with this type grain boundary should have good Jc values.

Figure 6(a) shows the effect of initial distribution of nucleated crystals and composite particles. Y123 crystals with c- and a-axed orientations and 45-degree from c-axis are growing from the liquid + particles which have another distribution pattern different from the above one. The shapes of Y123-grains and their meandered boundaries are different from the above case because of the different initial distributions of particles. Figure 6(b) shows simulated growth process for the case of less c-axis and a-axis crystals on the substrate. In this case, since crystals met each other after long length growth, small liquid pools with Ba-Cu rich phases are trapped at their interface. It is known that Jc of this type sample has lower than the former type samples [19]. Figure 6(c) shows a-axis crystal growth from the surface of the substrate. This crystal is growing large because of its sufficient time to grow, and finally will have inverse triangle shape. However, we hardly find this kind of triangle crystal. Therefore, it is considered that the growth rate of the crystal which reached at the surface of the film may slow down to make a slim a-axis crystal. The simulated result for the film with this change of growth rate is shown in figure 6(d), which looks similar to the experimentally observed many results.

5. Conclusions
Growth process of faceted Y123 crystals in YBCO film on LAO or CeO2/LAO in the modified TFA-MOD process was studied, and the following results were obtained.

(1) Growth processes of Y123 crystals in YBCO film with some process-controlling parameters were experimentally clarified on the basis of the observed results obtained by quenching the film during the firing process.

(2) The macro/micro-combined model was used to simulate the growth process of faceted crystals. The growth rate Vc(c-axis) and Va(a-axis) of Y123 crystal were assumed to be functions of the angle between the interface and facet plane.

(3) Growth processes of c-axis and/or a-axis oriented Y123 crystal grains under the various initial conditions such as initial distributions of nucleated 123 crystals and particles in the films were simulated and their growing behaviors were visualized.

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References
[1] McIntyre P C, Cima M J, Smith Jr J A, Hallock R B, Siegal M P, Phillips J M 1992, J. Appl. Phys., 71, 1868
[2] Fuji H, Honjo T, Nakamura Y, Izumi T, Shiohara Y, Teranishi R, Yoshimura M, Iijima Y, Saitoh T 2002, Physica C, 378–381, 1013.
[3] Shibata J, Tokunaga Y, Teranishi R, Fuji H, Honjo T, Izumi T, Shiohara Y 2003, Physica C, 392–396, 922
[4] Tokunaga Y, Fuji H, Teranishi R, Shibata J, Asada S, Honjo T, Izumi T, Shiohara Y, Iijima Y, Saitoh T 2003, Physica C, 392–396, 909
[5] Manabe T, Yamaguchi I, Nakamura S, Kondoh W, Kumagai T, Mizuta S 1995, J. Mater. Res., 10, 1635
[6] Smith J A, Cima M J, Sonnenberg N 1999, IEEE Trans. Appl. Supercond, 9, 1531
[7] Honjo T, Fuji H, Nakamura Y, Izumi T, Shiohara Y, Shibata J, Yamamoto T, Ikuhara Y, Teranishi R, Yoshimura M 2002, J. Jpn. Inst. Metal, 66, 151
[8] Tokunaga Y, Fuji H, Teranishi R, Matsuda J, Asada S, Kaneko A, Honjo T, Izumi T, Shiohara Y, Yamada Y, Murata K, Iijima Y, Saitoh T, Goto T, Yoshinaka A, Yajima A 2004, Physica C, 412–414, 910
[9] Teranishi R, Fuji H, Honjo T, Nakamura Y, Izumi T, Shiohara Y, Shibata J, Yamamoto T, Ikuhara Y, Yoshimura M 2002, Physica C, 378–381, 1033
[10] Minei T, Tanaka T, Ogata M, Mori N, Yamada Y, Mukaida M 2006, Physica C, 445-448, 570
[11] Honjo T, Nakamura Y, Teranishi R, Tokunaga Y, Fuji H, Shibata J, Asada S, Izumi T, Shiohara Y, Iijima Y, Saitoh T, Kaneko A, Murata K 2003, Physica C, 392–396, 873
[12] Shibata J, Honjo T, Fuji H, Araki T, Hirabayashi I, Hirayama T, Izumi T, Shiohara Y, Yamamoto T, Ikuhara Y 2002, J. Mater. Res., 17, 1266
[13] Solovyov V F, Wiesmann H J, and Suenaga M 2001, Physica C, 353, 14
[14] Mori N and Ogi K 2001, Meter. Trans., 42, 220
[15] Mori N and Ogi K 2002, J. Japan Inst. Metals, 66, 634
[16] Mori N and Ogi K 2005, Materials Transactions, 46, 930
[17] Yasuda H and Ohnaka I 1999, Proc. of Modeling of Casting and Solidification Processes VI (MCSP VI), 117
[18] Nastac L 1999, Proc. of Modeling of Casting and Solidification Processes VI (MCSP VI), 31
[19] Solovyov V H, Wiesmann H J, Li Q, Welch D O, and Suenaga M 2006, J. Appl. Phys., 99, 013902
[20] Mori N, Tanaka T, Minei T, Yamada K, Mukaida M 2007, IEEE Transactions on Applied superconductivity: Accepted for future publication, 99