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Growth rate limiting mechanisms of $\text{YBa}_2\text{Cu}_3\text{O}_7$ films manufactured by ex situ processing

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Abstract

$\text{YBa}_2\text{Cu}_3\text{O}_7$ films were fabricated on SrTiO_3 substrates using the BaF_2 ex situ process. Precursor films 1, 3 and 5 μm thick were processed in an atmospheric pressure reactor using a gas mixture of oxygen, nitrogen and water vapor. The films were processed at different water vapor pressures and it was observed that the film growth rate was independent of film thickness and proportional to the square root of the water vapor pressure. The dependence of the film growth rate on film area was also investigated for film areas varying from 10 to 160 mm^2 . Surprisingly, it was observed that the growth rate was inversely proportional to square root of the area of the film. A theoretical model is developed and applied to the experimental results presented in this paper. The model correctly predicts the inverse square root dependence of the film growth rate on sample area. In addition, it predicts that it will be difficult to process long samples, such as tapes, in simple reactor geometries. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) has demonstrated promising superconducting properties for use at liquid N_2 temperature with critical current densities $J_c > 1 \text{ MA cm}^{-2}$ in self-field and an irreversible magnetic field of $\sim 7 \text{ T}$. Recent progress in the development of bi-axially textured YBCO on an oxide buffered flexible metal tape has opened up possibilities of making use of these properties for

the applications in electric utility and high magnetic field devices [1,2]. These composite conductors are presently made in meter long lengths with critical currents exceeding 200 A (at self-field and $\sim 75 \text{ K}$) for one centimeter wide tapes [3]. The fabrication processes for these conductors require methods such as ion-beam assisted deposition and pulsed laser deposition which may not be commercially viable for the manufacturing of long lengths of tape. A number of alternative deposition methods are currently under investigation for YBCO and the buffer layers. One of these is the so-called BaF_2 ex situ process for the deposition of YBCO. In this process, a precursor layer, which consists of fine grained Y, Cu, and BaF_2 , or possibly BaF_2 and oxides of Y and Cu, is first

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deposited on a substrate. This layer is then heated in a flowing atmosphere which contains an inert gas, a partial pressure of O_2 (~ 100 mTorr), and is saturated with H_2O vapor. An attractive aspect of this process is the separation of the deposition of the precursor layer from the heat treatment for the formation of the YBCO. This separation minimizes the requirements for in situ monitoring as well as allows the use of different methods for fabricating the precursor layers, e.g., electron beam evaporation and sol gel processes [4,6,7]. In previous work we have deposited the precursor layer at rates exceeding 10 nm s^{-1} and rates up to 100 nm s^{-1} appear feasible. In addition the heat treatment of the precursor layer can be performed in a single step. Because of these favorable attributes, this process for the deposition of YBCO layers has been extensively studied for the development of YBCO thin films [4–7]. More recently, this process is being studied for high current applications of YBCO coated flexible conductors with encouraging results at high critical current densities [8–10].

The application of YBCO conductors to electric power or high magnetic field devices requires very high engineering current capacities, $>1000 \text{ A cm}^{-2}$ as well as lengths greater than a few hundred meters long. This requirement poses two difficult demands on the processing of practical YBCO conductors, (1) relatively thick layers of YBCO, $\sim 5 \text{ }\mu\text{m}$ thick or greater, are required and (2) the rate of production or, alternatively, the duration of heat treatment should be within practical limits. This implies that the conversion rate of the precursor to YBCO should be greater than $\sim 0.5 \text{ nm s}^{-1}$ as compared to some currently reported growth rates, which are as low as $\sim 0.1 \text{ nm s}^{-1}$. In order to meet these challenging requirements, a thorough understanding of the growth kinetics of the YBCO conversion process is sorely needed. For this reason, we studied the microstructural details of the process of nucleation and growth as well as the rate limiting processes for the growth of YBCO from electron beam evaporated precursor films on $SrTiO_3$ single crystals [8,11,12].

In this article we report our experimental results and theoretical analysis of the processes limiting the growth rate of YBCO layers.

2. Experimental procedure and results

The precursor films of the stoichiometric composition required for YBCO formation were deposited on polished (1 0 0) $SrTiO_3$ substrates using electron beam evaporation for Y and Cu and thermal evaporation for BaF_2 . The heat treatment for the formation of $YBa_2Cu_3O_7$ from the precursor was performed in a quartz tube. The quartz tube was 5 cm in diameter and 1.5 m long. The specimen was suspended at the center of the tube at the end of a quartz specimen holder, which was inserted from the gas exhaust end of the furnace. The specimens were processed at a constant temperature of 735°C under a flowing gas mixture at atmospheric pressure. The flow rate was $200 \text{ cm}^3 \text{ min}^{-1}$ (further in the text, unless stated otherwise, standard cubic centimeters are used for the gas flow) and the gas mixture consisted of 100 mTorr of O_2 , 25–150 Torr of H_2O with the balance being N_2 . The details of the precursor deposition and the heat treatment procedures were given in earlier publication [12]. Also, as previously described, the growth rates of the YBCO films were monitored in situ by measuring the conductance of the films. Since a precursor film becomes an insulator as soon as it is exposed to the processing environment and a YBCO film is semiconducting while it is growing, one can conveniently measure the growth rate by this method.

In Fig. 1, the time dependence of film conductance during the heat treatment is shown for films 1, 3, and 5 μm thick processed at water vapor partial pressure $p(H_2O) = 25$ and 150 Torr. As demonstrated earlier [8], the rate of change of the conductance is approximately constant with the processing period, implying that the growth rate of the YBCO film is approximately constant during the heat treatment. In addition, the growth rates are shown to be independent of film thickness from 1 to 5 μm at both partial pressures of H_2O . These results suggest that the solid-state diffusion of HF or H_2O through the precursor film is not the mechanism limiting the growth of YBCO, but rather a rate-limiting step is independent of the precursor film thickness [11].

If the growth rate is limited by the rate of HF removal from the film surface into the processing

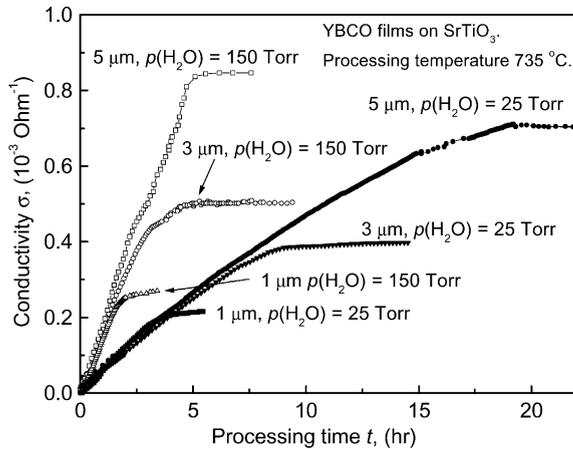


Fig. 1. Dependence of the YBCO/precursor film conductance on heat treatment time for 1, 3 and 5 μm films processed at 735°C. The results are given for two water vapor pressures, 25 and 150 Torr.

atmosphere, then the growth rate should be influenced by the size of the specimen. This is because the removal rate is controlled by the difference in HF partial pressure at the film surface, $p^s(\text{HF})$, and the ambient HF partial pressure, $p^a(\text{HF})$, in the chamber far removed from the film surface. This pressure drop is expected to take place over a distance approximately equal to the lateral dimensions of the specimen provided that the specimen size remains small compared to the chamber dimensions. Therefore, larger specimens would experience smaller pressure gradients and the HF removal rate, and by extension the growth rate, would be inversely dependent on the lateral dimension of the specimen.

In order to determine the dependence of the growth rate on the film size, we measured the growth rates for a set of approximately square films, where the areas varied from ~ 10 to 160 mm^2 . The smallest films, which were about 3 mm on a side, were cut from a single piece of a $3 \times 10 \text{ mm}^2$ precursor film. Films with larger areas were constructed by combining several $3 \times 10 \text{ mm}^2$ films into a composite sample with an approximately square pattern. In the case of a composite sample, the conductance during the heat treatment period was simultaneously recorded at both the “upstream” and “downstream” edges of the sample in order to measure the homogeneity of the

growth rate over the length of the specimen. For example, the observed difference in the growth rate from edge to edge was less than 10% for a composite specimen of five $3 \times 10 \text{ mm}^2$ substrates assembled into an approximate $12 \times 13 \text{ mm}^2$ rectangle. Also, we did not detect any influence of the carrier gas flow rates on the growth rate kinetics in the range of $100\text{--}500 \text{ cm}^3 \text{ min}^{-1}$. The carrier gas flow rate experiments were performed using $3 \times 10 \text{ mm}^2$ substrates with 1 μm thick YBCO films and were oriented such that the gas flow was directed over the 3 mm width.

The results of the measurement of the dependence of the YBCO growth rate, G , on the size of the precursor film area, S_F , is shown in Fig. 2. The YBCO films were processed at 735°C with oxygen partial pressure $p(\text{O}_2) = 100 \text{ mTorr}$, and water vapor partial pressure $p(\text{H}_2\text{O}) = 50 \text{ Torr}$. The solid line represents a fit to the data by a function $G \sim S_F^{-a}$ where $a \sim 0.5$. Since approximately square specimens were used, the growth rate is seen to be inversely proportional to the length of the edge of the precursor film.

In a previous publication we assumed that the reactions in Eq. (1) were only slightly shifted from chemical equilibrium and defined an equilibrium constant K relating the partial pressures of H_2O and HF. This is reasonable due to the very slow YBCO growth rates ($\sim 0.1 \text{ nm s}^{-1}$). In addition the

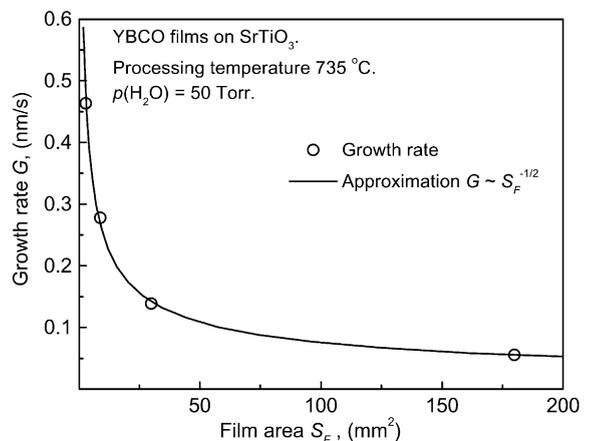


Fig. 2. Dependence of the growth rate, G , on the film area, S_F , at 735°C and 50 Torr water partial pressure. The solid line is fitted to the growth rate and given by $G \sim S_F^{-1/2}$.

partial pressure of HF, released from the reaction, is very small compared with the water vapor pressure present in the processing atmosphere. Based on these assumptions we concluded that the YBCO growth rate was limited by the removal of HF and correctly predicted the functional dependence of the YBCO growth rate, G , on the partial pressure of H_2O as $G \sim p(H_2O)^{1/2}$ [11] which was also observed earlier [8]. The model also presumed that the HF removal was limited by solid state diffusion through the unreacted precursor layer. Solution of the diffusion equation predicted the following time dependence of the YBCO growth rate: $G = A/(d_p^2 2At)^{1/2}$, where $A = 2KD_{HF}p(H_2O)^{1/2}$, d_p is the starting precursor layer thickness, D_{HF} is the diffusion constant of HF in the precursor and K is the equilibrium constant. The model predicted that the growth rate should be strongly time dependent, contrary to our earlier observations [8,9], see also Fig. 1. We speculated that the constant in time growth rate could possibly be explained in one of two ways. The precursor film might be infused with percolating channels. If the density of channels and the cross sectional area were large enough then the diffusion of HF would be governed by the approximate distance between the channels, d_{ch} , and the diffusion would be independent of the precursor film thickness. The second possibility was that the gas-phase diffusion of HF was rate limited at the film surface. In this scenario the growth rate would be dependent on film area in agreement with the growth rate dependence presented here, $G \sim S_F^{-1/2}$. This result, combined with our previous result, that the YBCO growth rate is independent of film thickness, is consistent with the idea that the growth rate is limited by the removal rate of HF, which in turn is limited by the rate of HF diffusion from the surface of the precursor film into the processing chamber. Below we present an analysis of the process of HF removal from the sample surface to the processing chamber atmosphere by means of gaseous diffusion and convection.

3. Theoretical analysis

In the following section the growth rate, G , of YBCO films is calculated by determining the re-

moval rate of HF from the precursor surface into the processing chamber. In order to provide a background for the discussion of the kinetics of YBCO formation we first summarize our previously reported studies on the microstructural development and the chemical reaction path for the formation of a YBCO layer. The growth rate is then determined in the limit of a small specimen (much smaller than the reactor cross-section) and a low flow rate of carrier gas. In this limit a significant simplification can be made in calculating the removal rate for HF. Moreover, the calculated results can be compared directly with our experimental results, since this limit also approximates our present experimental conditions. Since the calculated results for a small specimen have important implications for heat treating a long tape, we will also treat the case of a long tape, but still retain the condition of a low gas flow rate. It will be shown that under such conditions the growth rate becomes impractically slow for any lengths of the tapes, which are technologically meaningful.

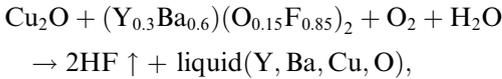
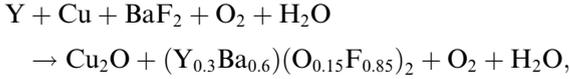
3.1. Chemical reaction path for the YBCO formation

Based on our experiments to date [11], we believe that the formation of a YBCO layer from an e-beam evaporated precursor film on $SrTiO_3$ proceeds according to the following steps:

- (1) In the initial stage of heat treatment, a new oxy-fluoride compound $(Y,Ba)(F,O)_2$ forms from the precursor, a fine grained mixture of Y, Cu, and BaF_2 .
- (2) YBCO grains nucleate at the surface of the (100) $SrTiO_3$ substrate with the YBCO c -axis perpendicular to the substrate surface.
- (3) After a continuous 50–100 nm layer of YBCO covers the substrate surface, a liquid layer forms separating the YBCO layer and the unreacted precursor.
- (4) Further growth of YBCO takes place by the dissolution of the precursor into the liquid and the precipitation of YBCO onto the existing YBCO layer.

One of the more important findings in our study of the mechanisms limiting YBCO growth is the fact that there is no detectable fluorine in the liquid

layer. However fluorine is present in the precursor in the ratio Ba/F = 1/2. This implies that the decomposition of the oxy-fluoride compound and subsequent release of fluorine takes place at the liquid–precursor interface. Based on these results, we hypothesized a chemical reaction path for the formation of YBCO as follows:



where the composition of the oxy-fluoride is an averaged value from a number of measurements at several locations in four films.

3.2. Small specimen limit

To calculate the growth rate, we first need to establish the nature of the gas flow at the sample, i.e. laminar or turbulent and the characteristic residence times. The YBCO processing is performed in a flowing gas and the process of the HF removal from the film surface into the ambient chamber atmosphere may be strongly influenced by the type of gas flow. The processing tube is 150 cm long and the sample is mounted on a cantilevered beam inserted along the central axis of the tube. The sample is positioned in the center of the processing tube and is located 2 cm from the leading edge of the cantilevered beam. The type of gas flow in the tube is determined by the Reynolds number, Re , defined as $Re = 2vxR_0/v$, where R_0 is the radius of the reactor and v and ν are the velocity and the kinematic viscosity of the processing gas, respectively. For Reynold's numbers less than 1200 the flow in the tube is always laminar and for numbers greater than 2200 the flow is always turbulent. The velocity is given by $v = F_t/\pi R_0^2$. F_t is the volume flow rate of a gas at an arbitrary temperature, $T(\text{K})$, where $F_t = FT(\text{K})/300$ and F is the measured volume flow rate. This correction to

the volume flow rate is required since the flow rate, F , is measured at room temperature ≈ 300 K. For the experiments reported here typical values of the gas flow rate are $F = 200 \text{ cm}^3 \text{ min}^{-1} = 3.33 \text{ cm}^3 \text{ s}^{-1}$ and the calculated temperature corrected velocity is $v = 0.57 \text{ cm s}^{-1}$. Taking the processing tube radius, $R_0 = 2.5 \text{ cm}$ and the kinematic viscosity, $\nu = 1.2 \text{ cm}^2 \text{ s}^{-1}$ at the processing temperature, 735°C , the calculated Reynolds number is $Re = 2.4$. This is much smaller than the Reynolds number required for the transition to turbulent flow and the gas flow in the reactor is laminar for the present case. At the entrance to the processing tube a boundary layer develops. At a distance from the tube entrance given by the critical entry length, $L_c = 0.07R_0Re = 0.42 \text{ cm}$ the boundary layer in the tube converges and the flow develops a parabolic velocity profile. When the gas flow reaches the leading edge of the cantilevered beam a new boundary layer develops. The boundary layer thickness, δ , for laminar gas flow is given by $\delta \approx 5x/(Re)^{1/2}$ where x is the distance from the leading edge of the beam.

The removal of HF from the film surface can be well described by the equation for the diffusion of HF in a steady state system in the laminar flow regime, i.e., [13]

$$D\nabla^2 p(\text{HF}) - v\nabla p(\text{HF}) = 0 \quad (2)$$

with the boundary condition of a constant partial pressure $p(\text{HF})^s$ over the film surface. D is the diffusivity of HF in the processing gas and the very small perturbation of the water vapor pressure is ignored. The spatial distribution of the gas velocity, v , may be found from the equations of momentum transfer in a laminar flow of gas. A complete solution of Eq. (2) is rather complex and requires a numerical method. However, as described below, the second term can be neglected when the flow of a gas is sufficiently slow over a small specimen. The second term is often called the convection term, but in the present case, is related to the removal of HF by the gas flow over the surface. In order to justify ignoring the convective term, it is sufficient to show that the time, τ_f , required to transport gas molecules across the specimen surface due to the bulk gas flow is much

greater than the time, τ_d , for the gas molecules to travel the same distance by the diffusion in the bulk gas.

For $x = 2.0$ cm, the distance to the edge of the specimen, $\delta = 6.45$ cm which exceeds the distance between the sample and the top of the tube furnace, ~ 2.5 cm, and the gas velocity above the sample can be approximated by $v(r) = v(1 - r^2/r_0^2)$ where $r_0 \approx 1.25$ cm. At a distance above the sample equal to the sample width, $W = 0.3$ cm, the flow velocity is 0.25 cm/s and the residence time, $\tau_r = W/v$, of the carrier gas over the specimen is 1.2 s. The time required for HF gas molecules to diffuse the same distance, $\tau_d = W^2/D$, is 0.036 s with $D = 2.5$ cm² s⁻¹ where the extrapolated diffusivity for H₂O at atmospheric pressure and 735°C was used for HF. Thus, $\tau_r \gg \tau_d$, allowing us to neglect the second term in Eq. (2). The HF concentration profile and the mass flux, f_{HF} , may now be obtained from the solution of the Laplace equation, $D\nabla^2 p(\text{HF}) = 0$. Note that in omitting the second term in Eq. (2), we do not necessarily neglect the effect of the flowing gas in the removal of HF from the surface. The role of the gas flow is to determine the ambient or background HF partial pressure, $p(\text{HF})^a$, at the distance far away from the HF source, i.e., $d > W$.

While the diffusive flow of HF from the film surface into the processing gas is the mechanism for the removal of HF near the surface, the steady state HF removal rate is determined by the difference in the partial pressures of HF at the surface and at the distance away from the surface of the specimen, i.e., $\Delta p(\text{HF}) = p(\text{HF})^s - p(\text{HF})^a$.

As discussed above, reaction Eq. (1) is only slightly shifted from equilibrium. An equilibrium constant, K , can be defined relating the partial pressures of H₂O and HF at the interface of the unreacted precursor and the liquid where the decomposition of the oxy-fluoride takes place. Taking into account the experimental observation that the growth rate is independent of the growth rate on film thickness we assume that the impedance to the flow of these gasses through the precursor is much less than through the ambient gaseous atmosphere. That is, the H₂O and HF partial pressures at the surface of the specimen may be taken approximately equal to the partial pressures at the

interface and are related by the following relationship:

$$p(\text{HF})^s / [p(\text{H}_2\text{O})^s]^{1/2} = K \quad (3)$$

where $p(\text{HF})^s$ and $p(\text{H}_2\text{O})^s$ are the partial pressures of HF and H₂O at the surface, respectively. Also, we will assume that $p(\text{H}_2\text{O})$ at the surface and through out the chamber is constant since the amount of H₂O in the carrier gas, 25–150 Torr, is much higher than that of HF in the gas. This assumption will be justified below after we estimate $p(\text{HF})^s$.

In order to determine the growth rate, G , the diffusive flux of HF from a specimen was calculated using the tabulated solutions of Laplace equation, Eq. (2) without the convective term. We used the solution for the case of heat transfer from an isothermal object immersed in a thermally conductive media under an isothermal surface [14]. Making the obvious substitutions: temperature \rightarrow concentration, heat conductivity \rightarrow diffusion coefficient, the general solution for the net HF flux, Φ_{HF} , emanating from the film may be written as follows:

$$\Phi_{\text{HF}} = DS \Delta p(\text{HF}) / kT \quad (4)$$

where k is Boltzmann's constant, T is the processing temperature and S is the tabulated shape factor. The concentrations, n , are expressed as partial pressures using the relation $p = nkT$. The best approximation for S to our film geometry is one of a thin rectangular plate, with width W and length L , at distance $\gg L$ from the isothermal surface. For this geometry the shape factor found from the table in Ref. [14] is $S \approx 2\pi L / \ln(4L/W)$. Taking into account that only one surface of the film is emitting HF and $W \approx L$ for the present case, the shape factor may be approximated as $S \approx 3W$. In order to relate the total HF flux, Φ_{HF} , and the YBCO growth rate, G , we note that the area averaged flux, f_{HF} , of HF is given by $f_{\text{HF}} = \Phi_{\text{HF}}/W^2$. From the chemical relationship, Eq. (1), we note that the formation of a single unit cell of YBCO releases four fluoride ions, which form four HF molecules. The relationship between the YBCO growth rate and the flux of HF out of the film can be given as:

$$G = f_{\text{HF}}V/4 \quad (5)$$

where V is the volume of the YBCO unit cell, $\sim 10^{-22} \text{ cm}^{-3}$. Using Eqs. (4) and (5) the following expression for the growth rate is obtained:

$$G \approx 3VD[p(\text{HF})^s - p(\text{HF})^a]/4kTW. \quad (6)$$

The background HF pressure, $p(\text{HF})^a$, may be approximated in terms of the growth rate G from the known flux of HF molecules, which are diluted in the carrier gas having a flow rate F_t :

$$\begin{aligned} p(\text{HF})^a &= \Phi_{\text{HF}}kT/F_t = f_{\text{HF}}W^2kT/F_t \\ &\approx 4GW^2kT/VF_t. \end{aligned} \quad (7)$$

Combining these expressions, (Eqs. (6) and (7)), we find the growth rate to be:

$$G = 3VDK[p(\text{H}_2\text{O})^s]^{1/2}/4kTW(1 + \alpha) \quad (8)$$

where $\alpha = 3WD/F_t$. The growth rate in Eq. (8) is expressed in terms of the experimental variable $p(\text{H}_2\text{O})^s$ using the relationship in Eq. (3). Again, this prediction of the dependence of the growth rate on the square root of the partial pressure of H_2O is consistent with the earlier experimental observation [8]. There are two regimes for Eq. (8) depending on the value of α . If this parameter is much less than unity i.e. $\alpha \ll 1$ then;

$$G \approx 3VDK[p(\text{H}_2\text{O})^s]^{1/2}/4kTW. \quad (8a)$$

In the other limiting case, $\alpha \gg 1$;

$$G \approx 3VF_tK[p(\text{H}_2\text{O})^s]^{1/2}/4kTW^2. \quad (8b)$$

For $\alpha \ll 1$, the volume flow rate of HF removal from the sample surface by diffusion, $\sim WD$, is much slower than the removal of HF by the carrier gas flow, F_t , at a point far from the surface. In other words, the carrier gas flow is at a sufficient rate and the sample is sufficiently small so that the amount of HF, which is released from the surface region, is removed from the processing chamber as fast as it diffuses from the surface region. Thus, we have a condition, $p(\text{HF})^s \gg p(\text{HF})^a$ and the growth rate does not directly depend on the flow rate of the carrier gas. For the present case, $W = 0.3 \text{ cm}$, $D = 2.5 \text{ cm}^2 \text{ s}^{-1}$ and $F_t(735^\circ\text{C}) = 10 \text{ cm}^3 \text{ s}^{-1}$, we find $\alpha \approx 0.23$. Eq. (8a) is a valid approximation to the experimental conditions used

in this study. It correctly predicts the experimentally observed dependence of the growth rate G on the size of the specimen, i.e., $G \sim S_F^{-1/2} \sim W^{-1}$ as shown in Fig. (2). It is also consistent with the observation that variations of $100\text{--}500 \text{ cm}^3 \text{ min}^{-1}$ in the gas flow rate have no significant effect on the growth rate.

If the film area increases, such that $\alpha \gg 1$, the dilution and removal of HF by the carrier gas is insufficient to prevent build up of HF in the processing atmosphere. At this point $p(\text{HF})^a$ is the factor limiting HF removal. In this regime the growth rate is inversely proportional to the film area and depends linearly on the carrier gas flow as shown in Eq. (8b). Obviously, in the limit of a film with infinite area, the processing system would reach a state of chemical equilibrium and the film growth would stop.

In addition to providing a mechanism for understanding of the growth limiting kinetics for a YBCO film using the BaF_2 process, the model allows us to estimate the partial pressure of HF at the film surface using Eq. (8a) and the equilibrium constant in Eq. (3). For example, we obtain $p(\text{HF})^s \approx 20 \text{ mTorr}$ using a growth rate of $\sim 0.5 \text{ nm s}^{-1}$ (Fig. 2) for a 10 mm^2 film at $p(\text{H}_2\text{O}) = 50 \text{ Torr}$ and 735°C . Then, the corresponding equilibrium constant for the reaction $K(735^\circ\text{C})$ is $\sim 3 \times 10^{-3} (\text{Torr})^{-1/2}$. By obtaining values of K at different temperatures, one can calculate the free energy, the heat of reaction and other thermodynamic parameters of the reaction in Eq. (1). However, more direct and precise measurements of the equilibrium constant may be made by processing samples in an atmosphere with controlled partial pressures of HF.

3.3. Long tape limit

In the above analysis, we treated the problem of HF removal from the precursor surface and its effect on the YBCO growth rate, in the small specimen limit. For the experimental conditions used in this study Eq. (2) can be simplified by neglecting the second term and this simplification allows us to gain the valuable physical insight regarding the primary growth mechanisms for a YBCO layer using the BaF_2 process. However, the

processing of technological useful superconductors requires the heat treatment of long tapes. In this case, the second term in Eq. (2) cannot be neglected. In the following section we estimate the inhomogeneity of the growth rate for a long tape processed in a tubular reactor.

Consider the case of a long tape being processed in a tube where the tape is positioned on the axis of the tube. The tube axis is designated the x -axis and the carrier gas flows through the tube along the positive x -axis direction. HF is generated along the whole length of the tape. The inhomogeneity of the growth rate arises because the HF concentration increases in the direction of gas flow (positive x -axis direction). This elevates the background partial pressure of HF, $p(\text{HF})^a$, and this, in turn, retards the growth of the downstream portion of the tape. The consequence of this effect is reported as the inhomogeneous growth rate of the YBCO for tapes as short as ~ 10 cm [10,15].

We solve a one-dimensional version of Eq. (2), taking into account both convective and diffusive terms. The three-dimensional HF concentration profile is replaced by an average concentration, n , at a given x coordinate. This simplification provides an analytical solution, which will help in understanding the physics of the problem at hand. The ambient HF pressure in Eq. (2) is converted to the average molecular HF concentration, $n(x)$, using the relationship $p(\text{HF})^a = nkT$. The equilibrium HF concentration at the tape surface, according to Eq. (3), is $n_s = K[p(\text{H}_2\text{O})^s]^{1/2}/kT$ and the flux of HF molecules produced by a length of tape, dx , is $d\Phi = D(n_s - n)S$. We take an approximate value of the shape factor $S \approx dx/\ln(W/R) \approx dx$, where W is the tape width and R the reactor tube radius. Changes in the concentration due to the action of the source (generation of HF by the tape) is $dn/dt = d\Phi/dV$, where $dV = S_r dx$ is the volume of a section of the reactor of length dx and S_r is the cross sectional area of the reactor tube. Combining Eq. (2) with the source term we have:

$$Dd^2n/dx^2 - vdn/dx + D(n_s - n)/S_r = 0. \quad (9)$$

The x coordinate lies along the tube axis and the carrier gas flows downstream along the positive

x -axis direction. D and v are the diffusivity of HF and the carrier gas velocity, as before. The first term is the variation of n along the length of the tape due to the diffusion of HF and the second is related to the gas flow. The last term is the source term for HF, which is determined by the local growth rate of YBCO. Solving Eq. (9) for $n(x)$ gives:

$$n(x) = n_s - (n_s - n_0)e^{-x/\lambda} \quad (10)$$

where

$$\lambda = 2DS_r/[(F_t^2 + 4D^2S_r)^{1/2} - F_t] \quad (11)$$

and n_0 is the value of n at $x = 0$. Substituting the resulting $p(\text{HF})^a$ in Eq. (6), we find the dependence of the growth rate along the position of the tape to be:

$$G(x) = G_0 \exp(-x/\lambda) \quad (12)$$

where G_0 is the growth rate at the front end of a tape and is given by Eq. (8a). The parameter λ defines the approximate maximum length of tape, which can be processed for a given set of processing conditions and reactor geometry. Depending on the values of the gas flow rate, there are two limiting cases. In the limit of low flow, $F_t \ll F_0$, where $F_0 = 2DS_r^{1/2}$, $\lambda = S_r^{1/2}$, i.e. λ becomes equal to the radius of the tube and does not depend on the flow. In the other limit, $F_t \gg F_0$, $\lambda = F_t/D$. It is instructive to estimate the distance λ , along a tape, at which the growth rate will be reduced to $\sim 1/2$ of the value of the growth rate at the front end of the tape for a typical set of experimental conditions. For example, if we take the values used in this study, i.e., $R = 2.5$ cm, $D = 2.5$ cm² s⁻¹, and a gas flow rate, $F_t(735^\circ\text{C}) = 10$ cm³ s⁻¹ (at atmospheric pressure), this distance is only ~ 7 cm. Unfortunately our analysis predicts that the utilization of a simple reactor design, i.e. a long tape contained in a long small diameter processing tube, will not work. The growth rate will become impractically small even for rather short lengths of tape. Consider, for example, the processing of a 10 m long tape. Suppose that the maximum acceptable nonuniformity of the growth rate is $\sim 25\%$ from one end of the tape to the other. This requires $\lambda \approx 40$ m and the required volume

flow, F_t is 600 l min^{-1} . At this flow rate a standard size industrial cylinder of gas would empty in about 12 min. Innovative reactor designs will be required.

4. Conclusion

We have shown that the rate of removal of HF from the surface of a precursor film into the reaction chamber is the rate-limiting step in the growth of YBCO in the BaF_2 ex situ process. The data is well described by a model where the diffusion of HF in the processing atmosphere is the dominant transport mechanism. The fact that the growth rate $G \propto S_F^{-1/2}$ eliminates both diffusion through the unreacted precursor material and a surface barrier layer as the dominant impedance to HF transport.

The model also predicts that processing long tapes in a tubular reactor at atmospheric pressure will require inordinately large gas flows. Special measures will be required to overcome this difficulty. Finally, although the experimental results which were discussed here were for electron beam and thermally evaporated precursor films, the analytical results are applicable to the formation of YBCO from BaF_2 containing precursor films synthesized by other means such as the sol gel process.

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References

- [1] Y. Iijima, N. Tanabe, O. Kohno, Y. Ikeno, *Appl. Phys. Lett.* 60 (1992) 769.
- [2] X.D. Wu, S.R. Foltyn, P.N. Arendt, W.R. Blumenthal, I.H. Campbell, J.D. Cotton, J.Y. Coutler, W.L. Hulst, M.P. Maley, H.F. Safar, J.L. Smith, *Appl. Phys. Lett.* 67 (1995) 2397.
- [3] S.R. Foltyn, P.N. Arendt, P.C. Dowden, R.F. DePaula, J.F. Groves, J.Y. Coulter, Q. Jia, M.P. Maley, D.E. Peterson, *IEEE Trans. Appl. Supercond.* 9 (1999) 1519.
- [4] P.M. Mankiewich, J.H. Schofield, W.J. Skocpol, R.E. Howard, A.H. Dayem, E. Good, *Appl. Phys. Lett.* 51 (1987) 1753.
- [5] P.C. McIntyere, M.J. Cima, M.F. Ng, *J. Appl. Phys.* 68 (1990) 4183.
- [6] M.P. Siegal, J.M. Phillips, R.B. van Dover, T.H. Tiefel, J.H. Marchall, *J. Appl. Phys.* 68 (1990) 6353.
- [7] R. Feenstra, D.K. Christen, J.D. Budai, S.J. Pennycook, D.P. Norton, H.H. Lowndes, C.E. Klanbunde, N.D. Galloway, in: L. Corrae (Ed.), *Proceedings of Symposium A-1 on High Temperature Superconducting Films at the International Conference on Advance Materials*, North-Holland, Amsterdam, 1991, p. 331.
- [8] V.F. Solovyov, H.J. Wiesmann, L.-J. Wu, M. Suenaga, R. Feenstra, *IEEE Trans. Appl. Supercond.* 9 (1999) 1467.
- [9] J.A. Smith, M.J. Cima, N. Sonnenberg, *IEEE Trans. Appl. Supercond.* 9 (1999) 1531.
- [10] R. Feensta, et al., *Proceedings of US DOE Annual Peer Review Meeting*, July 26–27, 2000, p. 361.
- [11] V.F. Solovyov, H.J. Wiesmann, L.-J. Wu, Y. Zhu, M. Suenaga, *Appl. Phys. Lett.* 76 (2000) 1911.
- [12] V.F. Solovyov, H.J. Wiesmann, M. Suenaga, R. Feenstra, *Physica C* 309 (1998) 269.
- [13] W.M. Rohsenow, H. Choi, *Heat, Mass and Momentum Transfer*, Prentice Hall, Englewood Cliffs, NJ, 1961.
- [14] J.P. Holman, H. Choi, *Heat Transfer*, McGraw Hill, New York, 1986.
- [15] M.J. Cima, private communication.