Simulation of Solidification Structures of Faceted 123 Peritectic Crystals in Superconductive YBCO Oxide

Nobuyuki Mori and Keisaku Ogi

Dept. of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka 812-8581, Japan

Since the micro/macro-structures affect the critical current density \( J_c \) and the mechanical properties of superconductive YBCO oxides, the following numerical and analytical studies of solidification process of faceted 123 \((\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta})\) crystals from liquid + 211 \((\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta})\) phases are essential to clarify the solidification mechanism and improve the properties of YBCO. To clarify the effects of growth mode and conditions on the microstructures of 123 crystals, two-dimensional numerical simulation of faceted peritectic growth of 123 crystal was performed by considering (a) growth of 123 crystal, (b) melting of 211 particles in the liquid, and (c) solute diffusion in the liquid. The growth rate \( R \) of 123 crystal was approximated by: \( R = a_g \cdot \Delta T^2 \), where \( a_g \) was kinetic growth constant, and \( \Delta T \) was kinetic undercooling of faceted interface. The kinetic melting constant \((\Delta m)\) and superheating \((\Delta T_m)\) was also used for evaluation of melting rate of 211 phase. Solute distributions in the liquid during the 123 growth were calculated by FDM, and the distributions of residual 211 particles and liquid pools in the faceted 123 crystals were evaluated from the experimentally obtained log-normal distributions of 211 particles in the liquid of YBCO. The calculated results agreed well with the experimental ones. Transition of macrostructures from columnar to equiaxed 123 crystals in unidirectionally solidified YBCO was also studied experimentally and analytically. Critical transition conditions (relations of growth rate \( R \) and temperature gradient \( G \)) were calculated by equations obtained from nucleation and growth theories, and compared with experimental results.

(Received August 22, 2000; Accepted December 22, 2000)

Keywords: superconductor, YBCO, \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \), numerical simulation, peritectic reaction, solidification, nucleation, facet, microstructure, macrostructure

1. Introduction

High \( J_c \) of superconducting YBCO oxide is realized by its solidification structure: superconducting phase with few grain boundaries and finely dispersed normal particles which work as flux pinning centers. Columnar or single crystal structure of 123 phase can be obtained by unidirectional solidification of YBCO oxide. Therefore, many studies have been done on the properties and the solidification structures of YBCO with high critical current density \((J_c)\). However, only a few studies have been made on the mechanism of faceted peritectic growth and formation of 123 grain structures. Authors have studied the 123 growth mechanism by two-dimensional numerical simulation, which is the coupled method of our analysis on faceted peritectic growth and王(source name)Y's numerical method (an explicit control volume finite difference method). In this paper, numerical study on the effects of growth mode and conditions on the microstructures, and analytical study on the critical conditions to form grain structures are performed to clarify the formation mechanism of micro/macros-structures of 123 crystals.

2. Faceted Peritectic Growth Model of YBCO 123 Crystal

When faceted cellular or planar 123 crystal grows from liquid + 211 phases, many 211 particles are dissolved in the liquid ahead of the growing 123 interface, and some excess 211 particles are incorporated into 123 phase. The distribution functions of 211 particles in the liquid were approximated by log-normal distribution:

\[
f_{211}(\ln(r)) = f_{211}(1/(\sqrt{2\pi}\ln(s_g))) \exp\left[-(\ln(r) - \ln(r_m))^2/(2(\ln(s_g))^2)\right],
\]

where \( f_{211} \) is volume fraction of 211 particles in the liquid, \( r \) is radius of 211 particles, \( \ln(r_m) \) is arithmetic mean of \( \ln(r) \), \( \ln(s_g) \) is arithmetic standard deviation.

From the above experimental results, the following growth model was developed for the faceted peritectic growth of YBCO. Two kinds of meshes were used in the model as shown in Fig. 1 (a) Cellular and (b) Planar interfaces. In these figures, dotted lines show the original-elements in the absolute coordinates, which are used to give the experimental log-normal distribution of 211 particles in the liquid. The sizes of the elements were mainly 6 \( \mu m \times 6 \mu m \), or 4 \( \mu m \times 12 \mu m \), and the calculated regions were 156 \( \mu m \times 312 \mu m \), or 160 \( \mu m \times 320 \mu m \). Solid lines show the elements and mesh in the moving coordinates for the calculation of the solute distribution in the liquid. An explicit control volume finite difference method (FDM) was used to calculate the liquid composition in the two-dimensional numerical simulation model. The faceted interface passed through grid points. Each element (solid lines) was divided into two “sub-elements” by the above original element (dotted lines) to obtain the fractions and sizes of 211 particles, and the average liquid composition of the element was calculated by the above FDM.

Outline of the numerical simulation is given by the following steps (S1)–(S9) under the assumptions (A1)–(A10).

(S1) Input data: Sizes and numbers of elements of two kinds of meshes (original mesh and moving mesh), physical and solidification constants, time step \( \Delta t \), initial temperatures (obtained from the temperature gradient \( G \) and the initial interface undercooling \( \Delta T \)), liquid compositions, and distribution of 211 particles in the liquid (log-normal distribution).

(S2) Calculation of 123 growth rates at the interface elements as a function of undercooling evaluated with their liquid compositions \((C_{123})\) and temperatures.

(S3) Calculation of the average 123 growth rate \((R_m)\) of the facet, which is assumed to take a value to maintain the faceted
interface, by using the above growth rate of each interface element.

(S4) Calculation of new positions and temperatures of the interface, elements and sub-elements after $\Delta t$.

(S5) Mapping of liquid compositions in new elements estimated by a linear interpolation on values in old elements, and mapping of distribution of 211 particles in the sub-elements by the use of data in the original mesh.

(S6) FDM calculation of liquid compositions in the elements after $\Delta t$. Boundary conditions: No solute flow at the system boundary. Solute conservation at the growth interface.

(S7) Calculation of the fraction of 211 particles which melt to adjust the liquid composition ($C_{Lk}$) to the kinetic growth/melt composition ratio ($\Delta C_k/\Delta C_m$) for “interface elements”, and to the liquidus composition for “bulk elements”. If two sub-elements contain the different sizes of 211 particles, the liquid composition is assumed to be determined by melting of the smaller particles first, and then the larger ones. The growth of particles was ignored.

(S8) Repeating the above process from step (2) to step (7) until the end of calculation.

(S9) Presentation and saving of the calculated results.

The basic assumptions and relations for the numerical simulation:

(A1) The peritectic solidification of faceted 123 phase from liquid + 211 phase is composed of the three primitive processes: (a) Growth of faceted 123 crystal (driving force: $\Delta C_k$), (b) Melting of 211 particles in liquid ($\Delta C_m$), (c) Solute diffusion in liquid ($\Delta C_d$). Total driving force ($\Delta C_L$) for the peritectic reaction is: $\Delta C_L = \Delta C_k + \Delta C_m + \Delta C_d$ (Fig. 2). $\Delta C_L$ is given by: $\Delta C_L = \Delta C_t + \Delta C_s$, where, $\Delta C_t$ is supersaturation ($= \Delta T_{pc} (1/m_{L123} - 1/m_{L211})$) caused by the undercooling ($\Delta T_{pc}$) from peritectic temperature, $m_{L123}$ and $m_{L211}$ are the slope of liquidus of 123 and 211, respectively, and $\Delta C_s$ is surface energy effect of 211 particle in the liquid.

(A2) The normal growth rate ($R_k$) of a facet is approximated by the equation: $R_k = ag \cdot \Delta T_k^2$ where $ag$ is a kinetic growth constant, $\Delta T_k (\equiv T_{L123} (C_{Lk}) - T_i)$: kinetic undercooling from the 123-liquidus ($T_{L123} (C_{Lk})$), $C_{Lk}$: liquid composition at the interface, $T_i$: interface temperature. To incorporate the effects of the average probability of the growth centers (screw dislocation sites) of 123 phase and of the growth with multi-dislocations, the average $R_k$ for average $C_{Lk}$ are examined in the calculation.

(A3) The melting rate of superheated 211-particles in the liquid is also assumed to be given by the above equation with a kinetic melting constant (am) and superheating ($\Delta T_m$). The ratio (ag/am) was assumed to be a small value, since the melting rate ($R_m$) of particles must be much higher than the growth rate because of the large difference in growth/melting rates. To the surface energy on the equilibrium liquid composition ($\Delta C_s$) at the surface of 211 particle in the liquid is evaluated, and 211 particles are assumed to be spherical. $\Delta C_s = 2\Gamma / (r \cdot m_{L211})$, where, $r$ is the radius of 211 particle, $\Gamma (= \sigma / \Delta S_f)$ is the Gibbs-Thomson coefficient, $\sigma$ is the
211/liquid interface energy, $\Delta S_f$ is the volumetric entropy of fusion.

(A5) Two-dimensional solute diffusion in the liquid is calculated by FDM: $\frac{\partial C}{\partial t} = D \cdot \nabla^2 C$, with the boundary conditions: $\frac{\partial C}{\partial X} = 0$, $\frac{\partial C}{\partial Y} = 0$ at each field boundary.

$D$ is diffusion coefficient in the liquid, and $C$ is solute concentration in the liquid. For the first approximation, the main controlling process is assumed to be redistribution and diffusion of $Y$ as solute element.

(A6) Solute atoms necessary for the growth of 123 phase are supplied by melting of 211 particles with mass transportation in the thin liquid layer at the interface element as it proceeds ($R_x \cdot \Delta t$), and the following equation is obtained: $R_x \cdot \Delta t \cdot (C_{123} - C_{120}) \cdot (1 - f_{211 \text{ in } 123}) = R_x \cdot \Delta t \cdot (C_{211} - C_{120}) \cdot (f_{211} - f_{211 \text{ in } 123})$, where $C_{123}$: 123 composition, $C_{211}$: 211 composition, $C_{120}$: liquid composition at the interface, $f_{211}$: fraction of 211 phase in the liquid, $f_{211 \text{ in } 123}$: fraction of 211 phase in 123 phase.

(A7) The excess 211 particles remain in 123 phase, or dissolve further in the liquid according to the fraction of 211 for the peritectic reaction. When the ratio of $\Delta C_{123}/\Delta C_{120}$ at the interface deviates from the kinetic value (obtained from $ag/am$ and the relation $R_x \approx R_w$), the 211 particles melt further or increase in 123 phase to accommodate the liquid composition.

(A8) The composition of the liquid in an element apart from the interface depends on the radius of 211 particle, and some particles dissolve partially to maintain the equilibrium with the liquid.

(A9) When the kinetic undercooling becomes negative in an element, 123 phase stops growing in the element and the liquid phase will be incorporated in the 123 phase.

(A10) Diffusion in the solid was neglected.

3. Calculated Results and Discussion

3.1 Simulated results of microstructures for faceted peritectic growth of 123 crystals

The distributions of 211 particles and liquid pools in the faceted 123 phase are calculated from the experimentally obtained log-normal distribution of 211 particles in the liquid.$^6,12$ Table 1 shows physical constants and solidification constants used in the calculation.$^6,12,18,19,26-29$ The merit of the computer simulation is that the effect of “one of the factors” on the structure formation can be made clear by fixing the other factors, while the actual experiment cannot realize this condition. Therefore, we performed the computer simulation with the various conditions shown in Table 2. In these simulations, the distribution of 211 particles is a fixed factor ($r_m = 2.3 \mu m$, $ln(\sigma g) = ln(1.7)$). Some other factors are also fixed: e.g., $G = 20 (K/cm)$, $R_0 = 2.7 \times 10^{-7} m/s$ (initial solidification rate = moving rate of isotherm) etc.

Figures 3(a)–(c) show calculated results of faceted growth of hyper-peritectic YBCO ($f_{211} = 0.43(\pm 0.2)$, $r_m = 2.3 \mu m$, $ln(\sigma g) = ln(1.7)$) for various growth modes and conditions under the following parameters: the average $R_k (R_{av})$, $ag = 3.4 \times 10^{-3} m/s$, $ag/am = 0.01$, $D(1260 K) = 3.5 \times 10^{-10} m^2/s$, $\Gamma = 0.01 \times 10^{-6} m-K$, $G = 20 K/cm$. In Fig. (a) for cellular interface ($\Delta T = 20 K$), there are more liquid-pools (black) at the cell boundary and more 211 particles (white) at the cell center of 123 crystal (gray), which agree well with the experimental results.$^6,13$ These phenomena are attributable to the difference in the shape of solute diffusion layer at the cell tip (convex layer) and the cell boundary (concave layer); more solutes (Y) are available for the growth of Y123 in the former, and insufficient solutes (Y) are supplied in the latter. Further, some small liquid pools appear in the 123 crystal, which are attributed to the non-uniform distribution of 211 particles in the liquid ahead of freezing front. The above results indicate that the structure of faceted interface is affected by the local supersatulations (or undercoolings), which depends on the distribution of 211 particles in the liquid ahead of the faceted 123 interface. In Fig. (b) for flat-cellular interface ($\Delta T = 20 K$), there are less liquid-pools at the cell boundary than cellular interface (a). In Fig. (c) for planar interface ($\Delta T = 20 K$), there is no liquid-pool in 123 phase. From the above results, it is clarified that the liquid pools decrease at the boundary region of 123-cell when the angle between the faceted interface and the normal plane to the growth direction becomes smaller. In Fig. (d) for planar interface and high undercooling ($\Delta T = 30 K$), there are some liquid-pools in the 123 phase, since there is less time for dif-

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Fraction of solid ($f_{211}$)</th>
<th>Interface morphology</th>
<th>Undercooling $\Delta T (K)$</th>
<th>Pushing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyper peritectic</td>
<td>0.43(±0.2)</td>
<td>cellular</td>
<td>20</td>
<td>No</td>
</tr>
<tr>
<td>Peritectic</td>
<td>0.32(±0.2)</td>
<td>planar</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

$m_r = 2.3 \mu m$, $ln(\sigma g) = ln(1.7)$, $ag = 3.4 \times 10^{-3} m/s$, $ag/am = 0.01$, $D = 3.5 \times 10^{-10} m^2/s$, $\Gamma = 0.01 \times 10^{-6} m-K$, $G = 20 K/cm$, $R_0 = 2.7 \times 10^{-7} m/s$ (initial solidification rate = moving rate of isotherm)

Table 1 Physical constants and solidification constants.

<table>
<thead>
<tr>
<th></th>
<th>(YO$_{1.5}$)</th>
<th>(Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of 123 phase</td>
<td>$C_{123} (\text{mol}%)$</td>
<td>16.7</td>
</tr>
<tr>
<td>Concentration of 211 phase</td>
<td>$C_{211} (\text{mol}%)$</td>
<td>50.0</td>
</tr>
<tr>
<td>Concentration of liquid</td>
<td>$C_{L,F} (\text{mol}%)$</td>
<td>0.6</td>
</tr>
<tr>
<td>Liquidus slope of 123 phase</td>
<td>$m_{L,123} (\text{Kmol}%)$</td>
<td>100</td>
</tr>
<tr>
<td>Liquidus slope of 211 phase</td>
<td>$m_{L,211} (\text{Kmol}%)$</td>
<td>230</td>
</tr>
<tr>
<td>Gibbs-Thomson coefficient</td>
<td>$\Gamma (m-K)$</td>
<td>$0.01 \times 10^{-6} (-1 \times 10^{-6})$</td>
</tr>
<tr>
<td></td>
<td>(YO123)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(YO123 + Pt)</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td>$D (1260 K) (m^2/s)$</td>
<td>$0.001 \times 10^{-6} (-0.1 \times 10^{-6})$</td>
</tr>
</tbody>
</table>
Fig. 4 Calculated results of peritectic YBCO ($f_{2311} = 0.32(±0.2)$, $rm = 2.3\mu m$, $ln(g_s) = ln 1.7$, $R_{av}$, $ag = 3.4\times10^{-3}$ m/s, $ag/am = 0.01$, $\Delta T = 20K$, $D = 3.5\times10^{-10}$ m$^2$/s, $\Gamma = 0.01\times10^{-6}$ m$^{-2}$ K$^{-1}$, $G = 20$ K/cm). (a) Cell. Without pushing, $R = 0.17\mu m/s$ (calculated), (b) Planar. Without pushing, $R = 0.10\mu m/s$ (calculated), (c) Planar. Pushing, $R = 0.17\mu m/s$ (calculated).

This phenomenon occurred by the luck of solute at the cell boundary where 211 particles are all melted in the peritectic sample. Figures 4(b), (c) show the effect of 211-pushing at the 123 interface for peritectic YBCO ($f_{2311} = 0.32(±0.2)$, $rm = 2.3$, $sg = 1.7$). Figure 4(b) is a result for planar interface when no 211-pushing occurs (without 211-pushing). There is no liquid-pool in 123 phase, and calculated $R$ is $0.10\mu m/s$. Figure 4(c) is a result for planar interface where 211-pushing is assumed to occur. There are small diffusion layer ahead of freezing front, and calculated growth rate is $0.17\mu m/s$, which is larger than that of (b) growing at the same undercooling ($\Delta T = 20 K$). Also in this case, there is no liquid-pool in 123 phase. It is known that the pushing of particles by growing interface occurs when the particles are small. In this “pushing” model, 211 particles at the interface element always remain in the liquid, and never incorporated in 123 phase. Therefore the amounts of 211 particles in the interface elements increase with the advance of interface, and therefore the average width of diffusion layer at the interface decreases and the growth rate of faceted interface increases. The above results for relatively large particles could be applied to samples with smaller particles.
The above simulation is applicable just in the case that 123 crystals grow at a small growth rate with a smaller undercooling and no new crystals nucleate in the bulk liquid. However, when cooling rate becomes larger, it is known that the equiaxed crystal structures form by the nucleation of new crystals in the liquid, which cannot be considered in the above simulation.

When the critical condition to form equiaxed crystals is clarified, we will be able to develop the above growth model to the more general form, which include the nucleation phenomena of new crystals in the liquid ahead of freezing front. In the following section, we analyze the critical transition condition of macrostructures from columnar to equiaxed structure.

3.2 Macrostructure formation of 123 crystals (transition of 123 macrostructures from columnar to equiaxed crystals)

Figure 5 shows experimentally obtained relations between the cellular growth rate \( R \) of faceted 123 cells and undercooling \( \Delta T \) during unidirectional growth or zone-melting/growth of YBCO. These are hyper-peritectic and peritectic YBCO specimens which were melted or zone-melted and unidirectionally solidified with a temperature gradients \( G \) at controlled cooling rates or some constant pulling rates. In the figure, black squares are data of Mori et al.\(^6\) and white squares are data of Cima et al.\(^9\) and white circles are data of Endo et al.\(^21\). Data of \( R \) are obtained by experiments directly or by multiplying normal growth rate \( u \) by \( \sqrt{2} \) or \( \sqrt{3} \) from geometric relations of triangular pyramidal or triangular prism-like cell. The following approximate relation is obtained between 123 growth rate \( R (\mu m/s) \) of faceted-cell and undercooling \( \Delta T (K) \) from the peritectic temperature \( (T_p) \).

Cellular Growth rate (m/s): \( R = A_{gc} \cdot \frac{\Delta T_r^2}{\eta(T)} \) \( \text{and} \quad (A_{gc} = 1.9 \times 10^{-5}) \) (1)

Normal Growth rate (m/s): \( u = A_{gp} \cdot \Delta T_r^2 / \eta(T) \), \( (A_{gp} = 1.2 \times 10^{-5}) \) (2)

where, \( A_{gc} \) and \( A_{gp} \) are constants, \( \Delta T_r = \Delta T / T_p, \Delta T = T_p - T, \) \( T \) is temperature at the interface, \( T_p \) is peritectic temperature of 123 phase, \( \eta(T) \) (Pa-s) is viscosity of the liquid: \( \eta(T) = A_e \cdot \exp(E/RT) \), \( A_e \) and \( E \) are constants, \( A_e = 1.9 \times 10^{-11}, E_g = 26000, \) and \( T \) is temperature (K).\(^6,12,22,23\)

Figure 6 shows experimental and calculated CCT-curves of 123 crystal growth. Experimental data are obtained by measuring the relationship between the incubation times and the temperatures for nucleation of 123 equiaxed crystals, which are determined as the times and temperatures of the melt in which a tiny crystals \( (f_s = 0.1 \sim 0.01, f_s: \text{fraction of solid}) \) are discovered ahead of the growing 123 interface. For a relatively small sample in which only few crystals nucleate, the effect of sample volume (or sectional area) and “incubation time” to nucleate a crystal should be included to evaluate TTT or CCT curves. CCT-curves are calculated from TTT equation by the conventional method to evaluate the fraction of time at each temperature. Therefore, we used the following modified Johnson–Meih–Avrami equation, which is modified by considering the faceted growth of 123 crystal and the incubation time \( u_{inc} \) for a crystal nucleated in the liquid, and the calculated results are shown by solid lines in the figure.

\[
t = A \cdot \eta(T) \left\{ \frac{f_s}{\Delta T_r^6 \cdot T_r} \cdot \exp \left( \frac{B}{\Delta T_r^2 \cdot T_r^2} \right) \right\}^{1/4} + u_{inc} \]

(3)

where, \( \eta(T) \) is viscosity (Pa-s), \( f_s \) is fraction of solid, \( T_r = T / T_p, \Delta T = T_p - T, \Delta T_r = \Delta T / T_p, \text{and} \) \( A \) and \( B \) are constants.

The above equation is derived from the following nucleation and growth equations.\(^{22-25}\)

\[
N = A_o \cdot \frac{T_r}{\eta(T)} \exp \left( \frac{-B}{\Delta T_r^2 \cdot T_r^2} \right)
\]

(4)

The incubation time \( u_{inc} \) to nucleate a crystal is calculated

![Fig. 5 Relationship between growth rate \( R \) of faceted cell and undercooling \( \Delta T \) from the peritectic temperature \( (T_p) \) during unidirectional solidification of Y123 crystal. \( (R \text{ (m/s)} = A_{gc} \times \Delta T_r^2 / \eta(T), A_{gc} = 1.9 \times 10^{-5}) \).](image)

![Fig. 6 CCT diagrams of Y123 crystal growth for experimental data and calculated examples for \( G = 20 (K/cm), f_s = 10^{-10}, 0.01, \text{and} 0.1, S_p = 0.16 (cm^2) \).](image)
from \( I_s \) and the effective volume \( V_{se} \) for nucleation.

Incubation time (s):
\[
t_{inc} = 1/(I_s \times V_{se}) \tag{5}
\]

Effective volume for nucleation \( V_{se} \) is approximated by the following equation.
\[
V_{se} = S_0 \times (\Delta T_\gamma / G) \tag{6}
\]
where \( S_0 \) is the sectional area (m\(^2\)) of the sample, the term \( (\Delta T_\gamma / G) \) is effective sample length and the temperature range \( \Delta T_\gamma \) is assumed to be 1 (K).

Solid fraction \( f_s \) :
\[
f_s = C_0 \cdot I_s \cdot \int_{t_{inc}}^{t_f} (u \cdot (t - t_{inc}))^3 \, dt = C \cdot I_s \cdot u^3 \cdot (t - t_{inc})^3 \tag{7}
\]
where, \( C = C_0/4 \). From the above eqs. (2) and (7),
time \( t_f \) (s) for solid fraction \( f_s \) is:
\[
t_f = \left( \frac{f_s}{C \cdot I_s \cdot u} \right)^{1/4} + t_{inc} \tag{8}
\]

Therefore, eq. (3) is obtained by substituting \( f_s \) and \( u \) in the above equation, and \( A = (C \cdot A_n \cdot A_g^2)^{-1/4} \), where \( C = 1 \), \( A_n \) and \( A_g \) are the constants from eqs. (4) and (2). Since \( A_g \) has a value of \( 1.2 \times 10^{-5} \), \( A = 412, A_n = 2 \times 10^4 \) and \( B = 1.2 \times 10^{-3} \) can be obtained by the fitting of CCT-curve to the experimental data.

When the undercooling for the growth of 123 phase is equal to that nucleating new crystals and growing to a small value of \( f_s = 10^{-10}, 0.01 \), the equiaxed structure should form.\(^5\)

Therefore, the critical transition condition from columnar to equiaxed structure (the critical G-R relation) is obtained by equating \( \Delta T_s (\equiv \Delta T_\gamma \) in eq. (1) for cellular growth \( (A_{gc} = 1.9) \) to \( \Delta T_s (\equiv \Delta T_{gr}) \) of the above calculated CCT-curve by using eq. (3). At first, a \( G \) value is assumed to calculate \( t_{inc} \), since \( t_{inc} \) is a function of \( G \) expressed by eqs. (3), (5), and (6). Then the critical R-G relation is derived for various \( G \) values by using the relations \( \Delta T_{gr} = \Delta T_\gamma \) and \( V_c = R \cdot G \). Finally, only one \( G \) value can be selected by trial and error method, since \( G \) in the critical G-R relation must coincides with the \( G \) value used for the calculation of initial \( t_{inc} \).

Figure 7(a) shows the effects of growth conditions (\( G \) and \( R \)) on the morphology of the solidification interface of Y123 phase. Black marks are faceted cellular or plane interface, and white marks are equiaxed blocky interface. Squares are data of Mori et al., circles are data of Cima et al., and triangles are data of Shiohara et al. Calculated results are shown by solid lines for the samples with sectional areas: \( S_0 = 0.03, 0.05, 0.1, \) and 0.2 (cm\(^2\)), which include sectional areas of the experimental samples: Mori et al.'s\(^9\) samples (plate: sectional area: \( S_0 = 0.16 \) cm\(^2\), 0.6 cm \( \times \) 0.26 cm \( \times \) 3.0 cm), and Cima et al.'s\(^8\) or Shiohara et al.'s\(^3\) samples (rod: \( S_0 = 0.03 \) cm\(^2\), \( \phi 0.2 \) cm \( \times \) 7-12 cm). Two solid lines (of the same \( S_0 \)) show the results for \( f_s = 0.01 \), and 10\(^{-10}\) respectively. The result for \( f_s = 10^{-10} \) are calculated from \( t_{inc} \) which corresponds to the case that only one crystal nucleates and grows in the liquid ahead of freezing front. However, we can clearly find crystals in the liquid when they grew to \( f_s = 0.01 \) or more. Therefore, we show the results for \( f_s = 0.01 \).

This analysis is made as the first approximation assuming that \( \Delta T_\gamma = 1 \) (K) in eq. (6), that is, the nucleation region \( V_{se} \) is limited in the temperature range of 1 (K), where the temperature varied from \( T_s \) to the final temperature \( T_f \) (the interface temperature). The more practical and precise result (Fig. 7(b)) is obtained by evaluating the nucleation in the volume \( V_{se} \) where the final temperatures are \( T_i \) to \( T_i + 20 \) K \( (\Delta T_\gamma = 20 \) K\). In the calculation \( V_{se} \) is divided in 20 regions according to temperature \( (T_f : T_i + 1, T_i + 1 \to T_i + 2, \ldots, T_i + 19 \to T_i + 20) \), and the initial temperature \( T_s \) is applied to each temperature region. CCT curves are calculated with the following eq. (9), where \( \Delta T_f \) is the time interval to cool the temperature region at the rate of \( V_c \), \( n \) is the total number of divisions for the system to satisfy eq. (9), \( m \) is the number of divisions for the above nucleation volume \( V_{se} \), and \( t_{rif} \) is the time to reach \( f_s \) at each temperature in TTT-curve. In this precise estimation, \( A_{gc} = 2 \times 10^4 \) and \( B = 1.2 \times 10^{-3} \) are also obtained by fitting the estimated CCT-curve to the experimental data.
\[
\sum_{i=1}^{n} \sum_{j=1}^{m} \frac{\Delta t_j / \tau_{eq}}{m} = 1
\]  

(9)

The calculated results show good agreement with corresponding experimental data. Since calculated results show some differences by the difference in volume of sample, we should apply a different criteria to each sample group depending on the different sectional area (volume) as shown in the above figure. However, when the difference in volume is not so large, it is convenient to use larger samples’ criteria for the safety to avoid the formation of equiaxed crystals.

As the critical condition to form equiaxed crystals is clarified, we will be able to develop the faceted peritectic growth model for 123 crystals in the near future to the more general form, which include the nucleation of new crystals.

4. Conclusions

Formation of macrostructures and microstructures of unidirectionally solidified or zone melted/grown YBCO are analytically and numerically studied to compare with the experimental results, and the following results are obtained.

(1) The faceted peritectic growth of 123 crystal from liquid + 211 phases is analyzed by a two-dimensional numerical simulation. The microstructures (distributions of 211 particles and liquid pools) simulated with the diffusion coefficient: \( D = 3.5 \times 10^{-10} \text{ (m}^2 / \text{s)} \) and the growth constant: \( a_g = 3.4 \times 10^{-3} \text{ (m/s)} \) for the average-rate growth (average growth size model) are in good agreement with the experimental ones for various growth modes and conditions. Both \( \Gamma \)-value and the ratio of \( a_g / a_m \) show little influence on the calculated results.

(2) When the angle between the faceted interface and thermal isotherm becomes smaller, the liquid pools at the 123-cell boundary decreased. When the undercooling and the growth rate are large, sufficient solutes cannot be supplied to growing crystal, and liquid-pools increased in 123 phase. Samples with high Y-composition result in 123 crystals with less liquid pools.

(3) The growth interface morphologies of the 123 crystals are summarized, and the effects of growth rate (\( R \)) and temperature gradient (\( G \)) on the critical transition conditions from columnar to equiaxial crystal structures are calculated by an equation obtained from nucleation and growth theories. The calculated transition conditions for samples with each section size (volume) agreed well with the experimental results.

Acknowledgements

This work was supported in part by Grant-in-Aid for Scientific Research (C2), and Proposal-Based New Industry Creative Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

REFERENCES