Effect of Volume Fraction on Coarsening of Y$_2$BaCuO$_5$ Particles in Ba–Cu–O Melt

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The effect of the volume fraction of the solid phase ($V_f$) on coarsening phenomena of Y$_2$BaCuO$_5$ (Y211) particles in Ba–Cu–O melt has been investigated. The volume fraction was changed from 10% to 40% by means of controlling of the nominal composition. The size distribution depends on the nominal composition as well. In the samples with hyperperitectic composition ($V_f > 37\%$), two different size groups were recognized. On the other hand, it was not observed in the case of hypoperitectic compositions ($V_f < 37\%$). The coarsening rate constant ($K$) also strongly depends on $V_f$ and classified into two groups even in the hypoperitectic compositions. The samples with lower $V_f$ than 15% reveal a higher coarsening rate constants than those with higher $V_f$ than 20%. The phenomena were qualitatively explained by the difference of coarsening mechanisms. Although the zero $V_f$ assumption in a mean field model can be applied for the samples with lower $V_f$, it became difficult with increasing of $V_f$ and the diffusion mode for the coarsening is changed from the diffusion through a mean field liquid to those among particles.

(Received August 18, 2000; Accepted December 6, 2000)

Keywords: superconductor, YBCO, coarsening, Y211 phase, volume fraction

1. Introduction

Much effort to realize high superconducting characteristics have been paid in oxide superconductors since the discovery of high $T_c$ superconductors in 1986.$^1$ Especially, in order to obtain high-$J_c$ superconducting materials, the following factors should be attained: (1) high density, (2) elimination of weak link, (3) highly-orientated structure, (4) introduction of effective pinning center, and (5) optimization of oxygen content. The appropriate annealing after the growth can solve the factor (5). The melt processing techniques including directional solidification processes are suitable for achieving the factors (1), (2) and (3). Actually, many solidification processes such as zone melting process,$^2$–$^4$ MPMS$^5$ etc. succeeded in growing single dominated YBa$_2$Cu$_3$O$_y$ (Y123) crystals due to optimization of the growth conditions. In the solidification processing, the Y123 phase is crystallized by the reaction between Y$_2$BaCuO$_5$ (Y211) phase and the liquid phase, which is called as a peritectic reaction. Therefore, the situation of the Y211 phase in liquid should strongly affect the crystal growth of Y123. Here, we should consider, at least, the following factors as the Y211 situations; (a) volume fraction, (b) average size, (c) size distribution, and (d) shape of particles. Concerning factor (a), it can be basically controlled by the nominal composition of the sample. However, the coarsening phenomena in the liquid have to be considered to control factors (b) and (c). The factor (d) is essentially governed by the crystal nature and growth conditions. The factor (d) is also related to the coarsening phenomenon. Additionally, the Y211 particles in Y123 phase can play an important role as the pinning centers,$^5$ which is the factor (4) mentioned above. Then, the control of the situation of Y211, especially sizes, is the important factor for achieving higher $J_c$. Then, there have been some reports for the coarsening of Y211 in liquid. However, the almost of the reports have concerned about the sample which has the hyperperitectic compositions,$^6$–$^7$ because the objective is mainly the investigation for achieving high $J_c$. Recently, the new requirements have been proposed. It is the fabrication of the high density Y123 single domain crystal without Y211 phase, which is expected as not only the high quality target materials for the vapor deposition processing but also the electric device substrate if the high crystallinity is realized.

From the scientific point of view, the coarsening phenomena were theoretically analyzed by Lifshitz and Slyozov$^8$ and Wagner,$^9$ which is well known as the LSW theory. This model proposed the cubic law, and it qualitatively agrees with many experimental results. However, it is based on the assumption of the zero volume fraction of the particle phase. Then, many researchers have reported the effect of the volume fraction of the particles in the matrix.$^{10}$–$^{13}$ However, the predictions by the reports do not necessarily agree with each other.

In this paper, we have experimentally investigated the effect of the volume fraction on the coarsening of Y211 particles in liquid, especially focusing on hyperperitectic compositions, which have been little reported.

2. Experimental

The precursors with the five different compositions were prepared as the following procedure. At first, the appropriate ratios of BaCO$_3$ and CuO powders were mixed in an mortar. Then, the powders were calcined at 1153 K in air for 12 h and ground. This calcination treatment was repeated four times for homogenization. The necessary amounts of Y$_2$O$_3$ powder were added into the powders and mixed. The compositions used in this study were listed in Table 1. In this table, the volume fractions of the Y211 phase at 1346 K are estimated from the mole fractions of Y211 and Ba$_2$Cu$_3$O$_y$ phases using the equilibrium phase diagram as follows.$^{14}$ If the mole frac-
Table 1 Compositions used in this study.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Y : Ba : Cu</th>
<th>Volume fraction ($V_f$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_f10$</td>
<td>0.2 : 1.6 : 2.6</td>
<td>10%</td>
</tr>
<tr>
<td>$V_f15$</td>
<td>0.3 : 1.65 : 2.65</td>
<td>15%</td>
</tr>
<tr>
<td>$V_f20$</td>
<td>0.4 : 1.7 : 2.7</td>
<td>20%</td>
</tr>
<tr>
<td>$V_f30$</td>
<td>0.8 : 1.9 : 2.9</td>
<td>30%</td>
</tr>
<tr>
<td>$V_f40$</td>
<td>1.2 : 2.1 : 3.1</td>
<td>40%</td>
</tr>
</tbody>
</table>

Table 2 Necessary values to obtain the volume fraction of the Y211 phase in liquid.

- Density of Y211 phase ($\rho_{211}$) $5.0 \times 10^3$ (kg/m$^3$)
- Density of liquid phase ($\rho_L$) $5.5 \times 10^3$ (kg/m$^3$)
- Molecular mass of Y211 phase ($M_{211}$) $1.15 \times 10^{-3}$ (kg/mol)
- Molecular mass of liquid phase ($M_L$) $1.07 \times 10^{-3}$ (kg/mol)

The volume fraction of the Y211 phase in liquid phase is indicated as $g$, the volume fraction of the 211 phase ($V_f$) can be described as,

$$ V_f = \frac{M_{211}}{(1 - g) \frac{M_L}{\rho_L} + g \frac{M_{211}}{\rho_{211}}} $$

where $M_{211}$ and $M_L$ are the molecular weights of the Y211 and liquid phases, and $\rho_{211}$ and $\rho_L$ are the densities of those phases, respectively. The used values in this study are listed in Table 2.

The compositions were selected to change the volume fraction from 10 to 40% on the compositional tie line of Y211-Ba$_2$Cu$_3$O$_{6+\delta}$. The selected compositions are described on the phase diagram as shown in Fig. 1. The four kinds of hypereutectic composition were selected, which correspond to the $V_f$ from 10 to 30%. Additionally, one hypereutectic composition ($V_f = 40\%$) was prepared as a comparison. The powders were uniaxially pressed at 60 MPa into the pellets with 5 mm in diameter and 0.5 mm in thickness. The precursor pellets were placed on the MgO single crystal substrate, which has a characteristics of low chemical reactivity and low wettability with the solution. Then, the precursor pellets were inserted into a preheated box furnace at 1343 K, which is higher than the peritectic temperature ($T_p = 1278$ K in air). After holding in the heated furnace for different times from 800 to 12800 s, the samples were quenched by means of dropping into a coolant. The microstructure observation and compositional analysis were carried out by optical microscopy and electron probe micro-analysis (EPMA). The particle size was evaluated by the bowstring measurement analysis. The sampling number for the evaluation was experimentally determined by the condition of saturation of its standard deviation.

3. Results

The macro-segregation in the sample along the vertical direction due to the gravity was at first considered especially in the low $V_f$ samples, because the density of the Y211 phase is higher than that of the liquid phase and the apparent-viscosity of the liquid, which is determined by the intrinsic viscosity of liquid and the mixture effect with the solid, should be low in the low $V_f$ sample than those in the high $V_f$ sample. Then, the spatial distributions in the cross-section of the samples were investigated. Figures 2(a) and (b) show the cross sections of the samples of $V_f10$ and $V_f30$, both heated at 1343 K for 12800 s taken by optical microscopy. In the pictures, the white particles are the Y211 phase, the black matrix is Ba-Cu-O melt and the bottom black plate without white particles is MgO substrate. From this observation, the uniform distribution of Y211 phase was attained even in the lowest $V_f$ sample in this study ($V_f10$) and the longest holding time, which are both enhancing conditions for segregation. Therefore, it can be concluded that the macro-segregation due to gravity is negligible for the experimental conditions in this study.

Figure 3 shows the sampling number dependence on average diameters and standard deviations in the sample $V_f15$ heated for 800 seconds as an example for determination of the suitable sampling number for the evaluation of the Y211 average size. In this figure, the filled circles indicates the individual data point and the lines are the average value and the deviations. In this case, it can be recognized that the average value and the deviation are saturated over 150 measurement points. We determined the average value by this procedure.

Figure 4 shows the backscattering electron compositional images of $V_f10$, $V_f30$ and $V_f40$ with different holding times. The white particles were the Y211 phase and the black ma-

![Fig. 1 Schematic illustration of the Y211-Ba$_2$Cu$_3$O$_{6+\delta}$ quasi-binary phase diagram, the compositions of the specimens used in this work are plotted on the diagram.](image1)

![Fig. 2 Optical micrographs showing transversal sections of (a) $V_f10$ and (b) $V_f30$ samples heated at 1343 K for 12800 s.](image2)
trix is the solidified liquid phase. In all compositions, the Y211 particles were coarsened with increasing holding time. However, the following differences due to the different nominal compositions were found. The difference in size distribution for different nominal compositions was observed. In the sample of hyperperitectic composition (Vf 40), there are two groups in size. One is a lot of particles but finer than 1 μm in radius. The other is a few but large around 5 μm in radius. On the other hand, the finer particles could not be observed in the samples with hypoperitectic compositions (Vf 10 — Vf 30). Typical radius distributions of Vf 30 and Vf 40 were shown in Fig. 5.

From the coarsening rate point of view, the large difference between Vf 10 and Vf 30 was recognized. The coarsening rate of Vf 10 is much larger than that of Vf 30. In other compositional conditions, Vf 15 and Vf 20 were classified into a group of Vf 10 and Vf 30, respectively. The quantitative evaluations of the average radius using the method mentioned above were carried out. Here, according to the classical coarsening theory proposed by Wanger et al., the coarsening behavior limited by the volumetric diffusion can be explained by the following equation,

\[ r^3 - r_0^3 = K \cdot t \]

(2)

where \( t \) is the time, \( r \) is the average radius at time \( t \), \( r_0 \) is the initial average radius and \( K \) is the coarsening rate constant.

Then, the time dependencies of the cubed radius for the samples with different nominal compositions of Vf 10 — Vf 30 are plotted in Fig. 6. From these figures, the large difference of the coarsening rate due to different Vf can be observed. Additionally, the linear relationship between time and cubed radius can be seen in the samples of Vf 20 and Vf 30. However, the relations in the samples of Vf 10 and Vf 15 are changed with time. According to the eq. (2), the coarsening rate constant in Vf 20 and Vf 30 can be easily obtained as \( 1 \times 10^{-20} \) and \( 1.5 \times 10^{-20} \) (m³/s) respectively.

4. Discussion

4.1 Difference in size distribution for hyper- and hypoperitectic compositions

As shown in Figs. 4 and 5, although two size groups were observed in the sample with hyperperitectic composition, the finer group can not be recognized in the samples with hypoperitectic compositions. The difference is considered to be caused by the difference in the generating process of the Y211

<table>
<thead>
<tr>
<th>Vf10</th>
<th>Vf30</th>
<th>Vf40</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="800s" /></td>
<td><img src="image2.png" alt="800s" /></td>
<td><img src="image3.png" alt="800s" /></td>
</tr>
<tr>
<td><img src="image4.png" alt="3200s" /></td>
<td><img src="image5.png" alt="3200s" /></td>
<td><img src="image6.png" alt="3200s" /></td>
</tr>
<tr>
<td><img src="image7.png" alt="12800s" /></td>
<td><img src="image8.png" alt="12800s" /></td>
<td><img src="image9.png" alt="12800s" /></td>
</tr>
</tbody>
</table>

Fig. 4 Backscattering electron compositional images showing the polished surface of Vf 10, Vf 30 and Vf 40.
In the hyperperitectic composition, the liquid phase could not exist and Y211 can be equilibrated with Y123 in solid state at the lower temperatures than the peritectic temperature ($T_p$). When the temperature was elevated at higher than $T_p$, Y211 can be additionally generated from Y123 due to its decomposition. In the hypoperitectic compositions, the Y211 phase can not exist as an equilibrium phase at lower temperatures than $T_p$. Therefore, the latter way can only be permitted for Y211 generation in the hypoperitectic compositions. The Y211 phase in solid state in the former process is considered to be fine and this group of Y211 particles can be the finer group in $V_f$ 40 sample.

4.2 Estimation of coarsening rate constant

According to the Fig. 6, the coarsening rate constants with different nominal compositions were obtained from the slope in the time dependence of cubed radius and summarized in Table 3. As mentioned above, the dependencies in $V_f$ 10 and $V_f$ 15 are not necessarily on the liner relationships. The possibilities for the reason for the non-linear relationship in the time dependence of the cubed radius for $V_f$ 10 and $V_f$ 15 can be considered as the shape effect far from the spherical assumption, the effect of a facet and the necessary time for the quasi-steady state distribution in the liquid such as an initial transient etc. The further theoretical and empirical investigations are needed to clarify this exact reasoning for it. At least, the large facet shape can be recognized in the samples held longer time than 3200 s for both $V_f$ 10 and $V_f$ 15. Therefore, the rate constants were calculated using the data before the time for $V_f$ 10 and $V_f$ 15 in this study to discuss the reason for the difference from the behavior in $V_f$ 20 and $V_f$ 30. The values for $V_f$ 10 and $V_f$ 15 were dispersed in the order from $10^{-19}$ to $10^{-18}$ (m$^3$/s) as shown in Table 3. From the LSW theory, the rate constant $K$ is introduced as follows,

$$K = \left(\frac{4}{3}\right) \cdot \left(2\Gamma D\Omega / m_L\right)$$ \hspace{1cm} (3)

where $\Gamma$ is the Gibbs-Thomson coefficient ($\sigma / \Delta S$), $\sigma$ is the interfacial energy between the Y211 solid phase and the liquid, $\Delta S$ is the volumetric entropy of fusion, $D$ is the diffusivity of solute in liquid, $\Omega$ is the molar volume of the Y211 phase and $m_L$ is the liquidus slope of the Y211 phase. In these parameters, $\Omega$ can be obtained as 9.2 $\times$ 10$^{-5}$ (m$^3$/mol)$^{15}$ and $m_L$ was experimentally clarified as 4.3 $\times$ 10$^{-1}$ (K-m$^3$/mol)$^{14}$. Additionally, the approximated value of 1 $\times$ 10$^{-10}$ (m$^3$/s) was often used in many reports for $D$ value.$^{2,17}$ On the other hand, there have been few reports about $\Gamma$ for the Y211 phase with liquid. In our previous reports of analysis for the growth of the Y123 phase, the order of 10$^{-6}$ (K-m) for $\Gamma$ was used. However, the considered temperature in those reports was 100 K lower than that in this study. Then, we assumed to be larger $D$ and $\Gamma$ value as 3 $\times$ 10$^{-10}$ (m$^3$/s) and 3 $\times$ 10$^{-6}$ (K-m), respectively.

Table 3 Coarsening rate constants for different compositions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate constant (m$^3$/s)</th>
</tr>
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<tbody>
<tr>
<td>$V_f$ 10</td>
<td>8.9 $\times$ 10$^{-19}$</td>
</tr>
<tr>
<td>$V_f$ 15</td>
<td>1.3 $\times$ 10$^{-18}$</td>
</tr>
<tr>
<td>$V_f$ 20</td>
<td>1.0 $\times$ 10$^{-20}$</td>
</tr>
<tr>
<td>$V_f$ 30</td>
<td>1.5 $\times$ 10$^{-20}$</td>
</tr>
</tbody>
</table>
respectively. Using these values, the rate constant for LSW theory, which is based on the assumption of \(V_f = 0\), can be estimated as \(1.7 \times 10^{-19}\) (m³/s). This estimated value is in the same order with that of \(V_f/10\), which is the smallest \(V_f\) in this study. Considering both the volume fraction of \(V_f/10\) and the uncertainty in parameters, especially for the \(\Gamma\) value, it is recognized that the calculation can apply for considering the coarsening phenomenon in this system.

4.3 \(V_f\) dependence of coarsening rate constant

As mentioned above, the expectation by Lifshitz and Slyozov, and Wagner, which is called the LSW model, is based on the assumption of the zero volume fraction of the solid particle phase. Concerning the effect of the volume fraction on the coarsening behavior, Ardell proposed a modification of the LSW theory modifying the diffusion equation using a realistic geometry. After this report, many investigations on the mean field (MF) model have been carried out to clarify the effect. In almost all reports, although the normalized coarsening rate constant at \(V_f = 0\) is consistent with the prediction by the LSW theory. The difference in \(V_f\) dependency due to respective assumptions can be recognized. Recently, a new concept of communicating neighbor (CN) model was proposed by De Hoff. In this model, it is assumed that the solutes diffuse due to the concentration gradient in the matrix between the surfaces of particles, the most significantly different point between the MF and the CN models is the coarsening rate constant at zero volume fraction. The constant tends to zero at \(V_f = 0\) in the CN model, although the normalized constant in the mean field theory is 4/9. Here, the experimental results in Table 3 are plotted in Fig. 7 with the prediction by Ardell as an example of the MF model using the estimated value of \(K (V_f = 0)\) in this study and that by Nomoto et al. as that of the CN model. From this figure, the rate constant values in the lower \(V_f\) samples may follow the MF model and the values drastically change to lie on the CN model at higher \(V_f\) than 20%. From this tendency, it can be explained that the assumption of negligible \(V_f\), which is the MF model, can be applied in the lower \(V_f\) samples than 15%. On the other hand, the assumption can not be adopted with increasing \(V_f\), which leads to the decreasing the interparticle distances. Consequently, the coarsening mechanism was changed from the MF model to the CN model with increasing \(V_f\).

5. Conclusion

Through the investigations of the coarsening phenomena of the Y211 particles in the liquid with different volume fractions, the following results were obtained.

Two size groups, which are finer than 1 µm and around 5 µm in radius, were observed in the sample with hypoperitectic composition. The finer size group can not be observed in hypoperitectic compositions. The difference can be explained by the difference in the generation process of Y211 during heating.

On the coarsening rate, the behaviors are classified into two groups on \(V_f\) even in hypoperitectic composition. The linear relationship can be observed in the samples with \(V_f\) of 20% and 30% in the time dependence of the cubed radius, while coarsening rate in the sample with samples with \(V_f\) of 10% and 15%.

The coarsening rates in the sample with 10% and 15% of \(V_f\) were much higher than those in the samples with \(V_f\) of 20% and 30%. The behavior of \(V_f\) dependence of the coarsening rate can be explained by the change of the coarsening mode. In lower \(V_f\) samples, the assumption of \(V_f = 0\) in the LSW model can be applied and a modified mean field model is suitable for the explanation. However, it becomes difficult with increasing \(V_f\). Then, the coarsening mode may transfer from the MF model to the CN model, which are governed by the direct diffusion among particles.

Acknowledgement

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) as a part of its Research and Development of Fundamental Technologies for Superconductor Applications Project under the New Sunshine Program administrated by the Agency of Industrial Science and Technologies M.I.T.I. of Japan.

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