Non-steady state solidification of superconducting oxides

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Received 13 June 1999

Abstract

The non-steady state solidification of RE123 (RE = Y, Nd) superconductive oxides was investigated by using an undercooling growth method. In both the Y- and Nd-systems, RE123 crystals grew steadily in the initial growth stage, but the growth rates decreased gradually in the later stage under the constant growth temperature. In the case of Nd-system, the substitution ratio of Nd/ Ba in the grown Nd123 crystal was found to be gradually changed. The liquid compositions revealed that the liquid composition was close to the ternary equilibrium point after the growth rates decreased. This non-steady growth of Nd123 crystal is intrinsically caused since the composition of grown Nd123 solid solution is not on the 422-123 line and the residual liquid composition gradually shifts to the ternary equilibrium point to compensate for the mass balance during 123 growth. On the other hand, in the case of the Y-system, the evaluation of the volume fraction of Y211 particles showed that the volume fractions in the grown crystal were lower than those expected from the initial composition. On the contrary, those in liquid were higher and had similar values irrespective of the initial compositions and growth conditions. This accumulation of 211 phase particles near the 123/liquid interface would reduce the diffusion of the solute elements, which have the partition ratio of less than unity, away from the 123 interface. Therefore, such a large volume fraction would enhance the compositional shift close to the growth interface and cause locally a final transient to decrease the growth rate of the 123 crystal, if there is a compositional shift from the line connecting 123 and 211 compositions. © 2001 Published by Elsevier Science Ltd.

Keywords: Non-steady state growth; Superconducting oxides; Undercooling method; Compositional shift; Isothermal growth

1. Introduction

The melt and growth process [1–3] is recognized as being effective for attaining a high critical current density \(J_c\) for practical applications of REBa\(_2\)Cu\(_3\)O\(_y\) oxide superconductors (RE123, RE = Y, Nd, Sm,…), since it enables one to grow large and highly oriented textures, which reduce a weak link problem. It is also effective in introducing high temperature stable phase (RE\(_2\)Ba\(_2\)Cu\(_3\)O\(_y\); RE211) particles into the RE123 phase matrix as strong magnetic flux pinning sites through peritectic solidification of the RE123 crystals. An important factor to improve \(J_c\) values is the usage of materials with higher superconducting transition temperatures \(T_c\), such as RE\(_{1-x}\)Ba\(_x\)\(_{2}\)Cu\(_3\)O\(_y\) (RE = Nd, Sm). RE123 (RE = Nd, Sm) oxides that have relatively large radii of RE ions, are solid solutions due to the substitution of RE ions at Ba sites, but have the problem of decreased \(T_c\) with increase in the substitution ratio. It is, therefore, crucial to control the substitution ratio for obtaining bulk RE123 crystals with high \(T_c\) and \(J_c\) values. Recently, it has been reported that the Nd123 crystals can exhibit higher \(T_c\) and \(J_c\) values in high magnetic fields at 77 K than those of Y123, when they are grown via melt processing under a low oxygen partial pressure [4–6]. Recent investigations revealed that the substitution of these crystals were suppressed, since the substitution range of Nd123 solid solution is very narrow under the low oxygen partial pressure in the study on the phase diagram [7].

Phase diagrams are useful for optimizing the parameters used to fabricate materials and for understanding the solidification mechanism. Fig. 1 shows the schematic quasi ternary phase diagrams in the Y- and the Nd-systems [7–11]. As shown in Fig. 1(a), since the Y123 phase is a stoichiometric compound, any liquid composition coexists with only one solid composition of the Y123 phase. Fig. 1(b) and (c) show the schematic phase diagram in the Nd-system under 0.01 and 0.21 atm oxygen partial pressures, respectively [7,11]. As shown in Fig. 1(b), the substitution range in Nd123 solid solution is very narrow and the Nd123 phase with a small substitution ratio can be grown from any liquid composition similar to the Y-system. On the other hand, as shown in Fig. 1(c), every liquid composition equilibrates with its...
corresponding Nd123 solid solution phase in air, when the initial composition is in the Nd123–liquid two phase region. The composition of the Nd123 phase grown from the liquid is, therefore, determined by the liquid composition and the growth temperature according to the equilibrium tie-lines. This speculation, in turn, indicates that a smaller substitution content can be obtained by optimizing the liquid composition, which makes it possible to attain higher $T_c$ values for melt processing in air.

RE123 superconducting oxides solidify through a peritectic reaction between a higher temperature phase and the liquid phase. The reaction is governed by solute diffusion in the liquid phase. Solidification models based on this idea were suggested by different research groups at almost the same time [12–14]. This idea can explain the basic phenomena about the solidification behavior in RE123 superconducting materials. In addition, several other important concepts, such as the pushing/trapping of the high temperature stable phase particles [15] and the effect of the solid solutions, must be considered to understand the growth mechanism of the system in further details.

In this paper, recent progress of the study in solidification behavior for RE123 superconducting oxides, especially for non-steady state growth, is reviewed using the result of an investigation into the crystal growth of bulk materials for RE123 superconducting oxides.

2. Experimental

The bulk growth of RE123 crystals were carried out by the following seeding and undercooled growth method. The Y- and Nd-123 systems were investigated in this study. Raw materials of RE$_2$O$_3$ (RE = Y, Nd), BaCO$_3$ and CuO were mixed and calcined twice to prepare the precursor powder with appropriate compositions such as RE:Ba:Cu = 1.8:2.4:3.4. Ba-enriched compositions were also prepared in the Nd system, and 0.5 wt% Pt powder was mixed after calcination in the Y-system. The precursor powder was uniaxially pressed into a pellet of 20 mm diameter and about 7–10 mm thickness. The sample pellets, placed on an MgO single crystal substrate in a furnace were heated to the maximum temperature of 1150°C. After holding at the temperature of 1150°C for 1 h, the samples were cooled to the seeding temperature and the seed crystal was placed on the sample surface. After seeding, the samples were rapidly cooled to the growth temperature ($T_g$), which is below the peritectic temperature ($T_p$), and held for predetermined growth times ($t_g$). Finally, the samples were quenched by dropping them into a coolant. The temperature was monitored with three sets of thermocouples placed close to the samples to confirm isothermal conditions around the sample. The growth length, microstructure, and compositional distributions of the samples were observed by using an optical microscopy and EPMA (electron probe micro analyzer). Since the
crystal size in the \(ab\)-plane (see Fig. 2) is important for the superconducting current loop in bulk applications, the growth characteristics were studied mainly in the \(a\)-direction.

3. Results

3.1. Growth behavior of Y123 crystal

Fig. 2 shows a typical top view of the melt grown sample. The Y123 crystal was grown epitaxially from the Nd123 seed crystal. The growth lengths were measured for the RE123 crystals grown under different conditions and were defined as the distance from the edge of the seed crystal to the 123/liquid interface. Fig. 3 shows the relation between the growth length and the growth time under the different growth conditions in the Y-system. At the early stage of crystal growth, the growth lengths increase in proportion to the growth time under all conditions. The growth rate, which is represented as the slope of the plotted line, is almost constant for growth times of less than \(10^5\) s. The growth rates of the Y123 crystals grown at larger undercooling \((T_s = 99^\circ C)\) were higher than those of the crystals grown at 1005\(^\circ C\). This dependence of the growth rate on undercooling is reported by Endo et al. [16] for steady-state

Fig. 3. The relation between growth length and growth time in the Y-system.

Fig. 4. The evaluated volume fraction of Y211 in the sample with 40 mol\% excess Y211 as a function of distance from the seed crystal.
solidification. The growth rate evaluated from Fig. 3 during the early stages of growth are in good agreement with the results of Endo et al. This indicates that steady-state solidification was achieved at the early stage of the Y123 growth. For growth times longer than 10’s, however, the growth rates were found to decrease in every crystal. Comparing the samples with 20 and 40 mol% excess Y211 contents, the growth rate of Y123 containing 40 mol% excess Y211 decreased earlier and the crystal size was also smaller than those with 20 mol% excess Y211, even though the growth rates were the same at the beginning of the solidification. These results indicate that the crystal growth of Y123 would depend not only on the undercooling, but also on the amount of the excess Y211 particles in the samples.

To clarify the effect of the Y211 particles on the growth Y123 crystals, the volume fractions of the Y211 particles were evaluated both in the Y123 solid and in the liquid regions for samples quenched during solidification at several growth times. The sample with 40 mol% excess Y211 quenched at a growth time of 98 h was examined using quantitative EPMA analysis. Fig. 4 shows the evaluated volume fraction of Y211 as a function of the distance from the seed crystal. As shown in this figure, the volume fraction in Y123 crystal was lower than that expected from the initial composition and gradually decreased with distance from the seed. On the other hand, the Y211 volume fraction in the liquid was higher than the expected from the initial composition. This phenomenon was explained by particle pushing/trapping behavior; that is, the Y211 particles were pushed by the growing Y123 interface and accumulated in the liquid. The decrease of Y211 volume fraction in the Y123 was also explained by the pushing/trapping theory as a decrease in the critical radius with decreasing growth rate [15].

Fig. 5 shows the distributions of Y211 in the liquid evaluated from quenched samples for which the Y123 crystal growth rates decreased remarkably, as indicated by the arrows in Fig. 3. The volume fractions in the liquid were higher than those expected from the initial composition and had a similar value of about 0.6 near to the interface, irrespective of the initial compositions and growth conditions. These results indicate that the Y211 particles pushed by the Y123 crystal were accumulated ahead of the Y123/liquid interface during solidification and were piled up in the liquid when the growth rates decreased.

3.2. Growth behavior of Nd123 crystal

Fig. 6 shows the relation between the growth length and growth time of the Nd123 crystal grown from sample with different initial compositions. The growth length of the Nd123 crystal increased linearly for growth time smaller than $2 \times 10^4$ s. Fig. 7 shows the temperature dependence of the growth rate for samples with different BaO/CuO ratios in this time range. The growth rate became smaller as the BaO/CuO ratio increased. The growth rate increased with decreasing the temperature for all samples; however, the change was different. The growth rate of the sample with the lowest BaO/CuO ratio depends strongly on the growth temperature, that is, higher growth rates were attained at lower growth temperatures. On the other hand, the increase in growth rate for a decreasing growth temperature is small for the samples with the highest BaO/CuO ratios. The difference in growth rates among the samples with different
Ba/O/CuO ratios increases with decrease in the growth temperature. Fig. 8 shows the growth time dependence of growth length of samples with different initial compositions for long growth times. The growth rates rapidly decreased for times greater than $3 \times 10^5$ s similar to the Y-system. Compared with the growth length of the Nd123 crystal before the growth rate decreased, the growth length of the sample with higher Ba/O/CuO ratio is smaller than that with the lower ratio.

Fig. 9 shows the substitution ratio of Nd123 crystal grown from the sample with the Ba/O/CuO ratio of 3/5 as a function of the distance from the seed crystal. In the initial growth stage, the Nd123 crystal with the substitution ratio of $x = 0.1$ grew about 400 µm. As the crystal grew, the substitution ratio gradually decreased, and finally the ratio becomes $x = 0.04$ after growing 1200 µm. From the substitution ratio of the Nd123 crystal, the liquid compositions can be evaluated using the tie-line information of the phase diagram in Nd-system [10]. Fig. 10 shows the evaluated compositions in the liquid equilibrated with the Nd123 crystal as a function of the growth time. The growth length is also plotted in Fig. 10. This figure clearly shows that the decrease in the growth rate correspond to the change of the liquid compositions as well as the Nd123 compositions. The liquid composition was found to be close to the Nd123–Nd422–liquid three phase equilibrium point after the growth rate had decreased.

4. Discussion

From the results of the growth experiments, both the Y123 and Nd123 crystals showed non-steady state growth behavior. Especially in the Nd-system, a compositional shift was clearly observed during growth in the liquid and in the
Nd123 solid solution. This suggests that the compositional shift caused the decrease in the growth rate and can be explained by consideration of the phase diagram.

Fig. 11 shows the route of compositional shift during the Nd123 growth on the quasi ternary phase diagram in the Nd-system at 1070°C [11]. When the Nd422 phase is presumed to be a stoichiometric compound, the initial liquid composition locally equilibrated with Nd422 is on the line connecting Nd422 and the initial composition. Assuming that the diffusivity of all elements is similar, solidified Nd123 crystal will have a composition determined by the equilibrium tie-line including the liquid composition equilibrated with Nd422 in the Nd123–liquid region. At this temperature, the solidified Nd123 crystal is a Nd-rich solid solution; that is, solidified Nd123 crystal does not exist on the line connecting the composition of the 422 and ‘035’ solution. As the result of the formation of Nd123 solid solution, the averaged composition of initially solidified Nd123–Nd422 crystal is on the tie-line connecting the initial Nd123 solid solution and the Nd422 (point α in Fig. 11) and the average liquid composition should, therefore, shift to the Ba-rich side from the initial liquid composition to maintain the mass balance condition (point α′ in Fig. 11). This means that the composition of the liquid should continuously shift to the Ba-rich side and the substitution ratio of solidified Nd123 crystal should, therefore, decreases as Nd123 crystal grows. At the end, the liquid composition moves to the Nd123–Nd422–liquid three phase equilibrium point and the Nd123 crystal with lowest substitution ratio should obtained. In addition, the compositional difference between the Nd123/liquid and Nd422/liquid interfaces becomes small when the liquid composition moves to the Ba-rich side and the difference
becomes zero at the ternary equilibrium point. Accordingly, the compositional difference between the interfaces decreases as growing the Nd123 crystal and the growth rate of crystal, therefore, decreases. Finally, when the liquid composition reaches the ternary equilibrium point, the 123 crystal does not grow but is in equilibrium. This means that the growth of Nd123 solid solution crystal is always non-steady state even if the initial composition is on the connecting 422 and 123 as usually selected in the Y-system.

In the case of the Y-system, when the initial composition is on the line connecting Y123 and Y211, the average compositions in the liquid and in the crystal will move on the line because of the pushing/trapping of Y211 particles at the interface. In this case, both average compositions move only on the Y211–Y123 tie-line and never get out from the line because of mass balance condition. The compositional difference between Y211/liquid and Y123/liquid is, therefore, maintained during solidification and Y123 crystal thought to be solidified up to the end of the sample keeping this condition. However, as shown in the previous section, the growth rate of Y123 crystal decreased considerably during Y123 growth and the volume fraction of Y211 solid in the liquid always had higher values than the initial volume fraction. If the average composition is always on the Y123–Y211 tie-line, it is hard to explain such a decrease in growth rate by consideration of the phase diagram. However, if the average composition gets off the Y123–Y211 tie-line for any reason, the growth rate will decrease similarly to the case of the growth in the Nd-system. The observation of piling up of Y211 particles near the Y123...
interface, after the growth rate decreased considerably, would suggest that such a high volume fraction of Y211 particles also plays some roles in the non-steady solidification. In ordinary diffusion solidification models for 123 growth, it was assumed that there is no interaction among Y211 particles. However, there are some interactions among Y211 particles such as the coarsening and the effective diffusion area in the liquid for providing or rejecting solute between Y123 and Y211 is also determined by the volume fraction of Y211 in the liquid. In the peritectic reaction of 123 growth, Y211 particles dissolve in the liquid near the 123 interface so the volume fraction of Y211 should decrease gradually near the Y123/liquid interface. At the same time, Y211 particles were pushed and accumulated in the liquid. There should be, therefore, a drastic change in Y211 volume fraction near the interface. The large volume fraction would decrease an effective solute diffusion away from the Y123/liquid interface because of the decrease of effective diffusion area in liquid and the interaction among the Y211 particles. In addition, the large volume fraction may cause the increase of actual diffusion path since the solute should diffuse around the 211 particles. These factors would have the effect of decreasing the effective diffusion coefficient. This image is shown schematically in Fig. 12. If a large volume fraction would act as an obstruction of solute diffusion away from the 123/liquid interface, the existence of a local boundary region near the interface may be assumed. The compositional shift to the three-phase equilibrium point will be enhanced easily in the local boundary region since the region may have a volume smaller than that of the whole sample. This may explain the reason why the growth rate of the Y123 crystal was decreased considerably. If a small compositional shift from the Y123–Y211 tie-line in the Y-system can be assumed for any reason, such small shift will be enhanced in the local boundary region and cause locally a final transient to decrease the growth rate of Y123 crystal. In a sample of the initial composition with a smaller excess amount of the Y211 phase, the Y123 crystal grew larger than that with a higher excess of Y211 content. This difference was caused by the difference of the necessary time for accumulation of the Y211 particles near the Y123 interface by pushing phenomena to reach the local final transient condition.

A similar discussion can be adapted to the Nd-system.
However, in the Nd-system, the compositional shift to the three-phase equilibrium point would be achieved in an earlier growth stage because Nd123 is the solid solution and has, therefore, the larger driving force for compositional shift. Accordingly, the necessary volume fraction of 422 is not so large in comparison with the case of Y123 growth as to cause the local final transient.

5. Summary

In both the Y- and the Nd-systems, the growth rate of RE123 crystals was initially almost constant and depended on the growth temperature. The growth rates decreased gradually in the later growth stages even at a constant growth temperature. In the case of the Nd-system, the substitution ratio of the grown Nd123 crystal was found to be gradually changed. The liquid compositions evaluated from the composition of Nd123 using tie-line information revealed that the liquid composition was close to the ternary equilibrium point after the growth rates decreased. This non-steady growth of Nd123 crystal is caused because the composition of grown Nd123 solid solution is not on the 422–123 line and the residual liquid composition gradually shifts to the ternary equilibrium point to maintain the mass balance during 123 growth. On the other hand, in the case of the Y-system, the evaluation of the volume fractions of Y211 particles showed that the volume fractions in the grown crystal were lower than those expected from the initial composition. Contrarily, those in the liquid were higher and had similar values irrespective of the initial compositions and growth conditions. This accumulation of the 211 phase particles near the 123/liquid interface would act as an obstruction to solute diffusion away from the 123 interface. Therefore, such a large volume fraction would enhance the compositional shift close to the growth interface and decrease the growth rate of 123 crystal, if there is an initial compositional shift from the line connecting 123 and 211 compositions.

Acknowledgements

This work was supported by New Energy and Industrial Technology Development Organization for the R & D Industrial Science and Technology Frontier Program.

References

[1] S. Jin, T.H. Tiefel, R.C. Sherwood, R.B. van Dover, M.E. Davis, G.W. Kammlott, R.A. Fastnacht, Phys. Rev. B 37 (1988) 7850.
[2] M. Murakami, M. Morita, K. Doi, K. Miyamoto, Jpn. J. Appl. Phys. 28 (1989) 1189.
[3] H. Fujimoto, M. Murakami, S. Gotoh, T. Oyama, Y. Shiohara, N. Koshizuka, S. Tanaka, Advances in Superconductivity, vol. II, Springer, Tokyo, 1990, p. 285.
[4] M. Murakami, S.I. Yoo, T. Higuchi, N. Sakai, J. Weltz, N. Koshizuka, S. Tanaka, Jpn. J. Appl. Phys. 33 (1994) L715.
[5] S.I. Yoo, M. Murakami, N. Sakai, T. Higuchi, S. Tanaka, Jpn. J. Appl. Phys. 33 (1994) L1000.
[6] S.I. Yoo, N. Sakai, H. Takaichi, T. Higuchi, M. Murakami, J. Appl. Phys. 65 (1994) 633.
[7] M. Yoshizumi, M. Kambara, Y. Shiohara, T. Umeda, Extended Abstract of International Workshop on Superconductivity in Hawaii, 1997, 295 pp.
[8] K. Oka, K. Nakane, M. Ito, M. Saito, H. Unoki, Jpn. J. Appl. Phys. 27 (1988) L1065.
[9] B.J. Lee, D.N. Lee, J. Am. Ceram. Soc. 74 (1991) 78.
[10] T. Aselage, K. Keefer, J. Mater. Res. 3 (1988) 1279.
[11] M. Kambara, T. Umeda, M. Tagami, X. Yao, E.A. Goodlin, Y. Shiohara, J. Am. Ceram. Soc. 81 (1998) 2116.
[12] T. Izumi, Y. Nakamura, Y. Shiohara, J. Mater. Res. 7 (1992) 1621.
[13] M.J. Cima, M.C. Flemings, A.M. Figaredo, M. Nakade, H. Ishii, H.D. Brody, J.S. Haggerty, J. Appl. Phys. 72 (1992) 179.
[14] N. Mori, H. Hata, K. Ogi, J. Jpn. Inst. Metals 6 (1992) 648.
[15] A. Endo, H.S. Chauhan, T. Egi, Y. Shiohara, J. Mater. Res. 11 (1996) 1996.
[16] A. Endo, H.S. Chauhan, Y. Nakamura, Y. Shiohara, J. Mater. Res. 11 (1996) 1114.