

## Effects of Precursor Powders on the Directional Growth of $\text{YBa}_2\text{Cu}_3\text{O}_x$ Superconductors

Tae-Hyun Sung\*, Sang-Chul Han\*, Young-Hee Han\*, Jun-Sung Lee\*,  
Eugene Kim\*\*, and Kwangsoo No\*\*

**Abstract:** Textured bulk  $\text{YBa}_2\text{Cu}_3\text{O}_x$  superconductor samples were grown directionally using different precursors of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  powder, and a mixture of  $\text{Y}_2\text{BaCuO}_5$ ,  $\text{BaCuO}_2$  and  $\text{CuO}$  powder. The microstructures and superconducting properties of the samples were compared. The mixture powder produced better microstructures i.e. dense and crack-free so that a higher critical current density was achieved at the same hot-zone temperature of  $1150^\circ\text{C}$  than the reacted powder does. When the reacted powder used as a precursor, as the hot-zone temperature increased upto  $1215^\circ\text{C}$ , the texture of the sample improved and the critical current density increased. The amount of melt in the sample is of secondary importance for the growth of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_x$  grains. The microstructures and superconductivity of good quality superconductors grown directionally were more strongly influenced by the kind of precursor rather than the amount of melt in a sample.

**Key Words:** superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , directional growth, precursor

### 1. Introduction

The melt-texturing technique is well known to be an excellent method for solving the weak-link problem and obtaining bulk high  $T_c$  superconductors with a high critical current density.

Among the fabrication parameters, the type of precursor is an important factor in determining the superconducting properties. Many studies have been reported that the directionally grown superconductors exhibited critical current densities of over  $10^4 \text{ A/cm}^2$  at the boiling point of liquid nitrogen. Melt texturing methods can be classified into three major categories [1]: (1) slow cooling without a temperature gradient, (2) slow cooling in a

temperature gradient without sample transport, and (3) slow cooling in a temperature gradient with sample transport. The directional growth used in this work is of type (3). Modifications were made to the melt texturing method to improve the microstructure and the transport properties of the melt textured superconductors. Such modifications include the variation of the type and stoichiometry of precursor powders [2] and addition of the second phases [3]. The hot-zone temperature (the maximum temperature in the temperature gradient) of our previous studies [2, 4] at which the maximum critical current density showed, was a few hundred degrees lower than in other's study [5]. A significant difference between these two studies was the kind of precursor powder used. Reference 5 used reacted  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (123) powder, but we used a  $\text{Y}_2\text{BaCuO}_5$  (211),  $\text{BaCuO}_2$  (011) and  $\text{CuO}$  (001) powder mixture. We speculated that the mixture powder used in our studies forms liquid at lower temperature, and that the liquid might decrease the melting temperature of samples, resulting in much enhanced a maximum critical current density.

In the present study, we fabricated  $\text{YBa}_2\text{Cu}_3\text{O}_x$  the samples grown directionally using two different precursor powders of reacted 123 powder and a 211+011+001 mixture powder. The microstructures and superconducting properties were examined and the difference of the two precursor powder were discussed.

### 2. Experimental procedure

Precursor powders of 123, 211, and 011 were synthesized using solid state reactions of reagent grade  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  powder mixtures. The processing conditions for the precursor powders have been described in detail in Ref. [6]. Precursor powders of 211, 011 and 001 were mixed at the stoichiometric ratio of 123 and ground using an automatic agate mortar and pestle for 1 h per each 10 g. Bar samples ( $\sim 0.2 \times 0.2 \times 3.5 \text{ cm}^3$ ) of the mixture powder and 123 powder with a few drops of organic binder were pressed in a steel mould. After drying in air overnight, the

\* 정 회 원 : 한국전력공사 전력연구원

\*\* 비 회 원 : 한국과학기술원 재료공학과

원고접수 : 1999년 3월 01일

심사완료 : 1999년 4월 20일

bar samples were carefully heat treated at 850°C for 1 hour to burn-out the organic binder and to densify. A small hole was drilled in one side of the bar sample in order to hang the sample on a constant speed puller using platinum wire. The bar samples were pulled up through a high-temperature zone provided by a small platinum coil inside a kanthal furnace. The pulling speed in this study was 1.2 mm/h. A schematic diagram and a typical temperature profile of the directional growth furnace was shown in Ref. [4].

After cooling down to room temperature, both surfaces of the bar samples were ground flat using SiC papers. Four electrical contacts on the samples were made using a silver paste. The samples were heat treated in oxygen flowing atmosphere at 800°C for 1 h to provide better contact between the superconductor and silver paste. And the sample was cooled to 550°C and held for 24 h in order to provide 123 with appropriate oxygen stoichiometry and then cooled down to room temperature.

The superconducting transition temperatures and the critical current densities of the samples were measured using the d.c. four point probe method. The lead wires carrying the current were attached to the silver contact using In-Ga eutectic liquid metal for critical current density measurements in liquid nitrogen. The voltage drop across the two inner electrical contacts was measured using a Keithley 181 nanovoltmeter, and the temperature measured using a Si diode attached to the back side of the sample and a Lakeshore 805 controller. The microstructure of the sample was observed using a polarized light microscope. An energy dispersive x-ray spectroscopy (EDXS) with a scanning electron microscope (SEM) was used to analyze the elemental composition of the constituent.

### 3. Results and discussion

Figure 1 shows the appearance of typical samples, of which the precursors are (a) 211+011+001 mixture powder (designated as the mixture powder sample in the present paper) and (b) reacted 123 powder (designated as reacted powder sample), grown directionally at the same hot-zone temperature of 1150°C (temperature gradient,  $G = 12.5^\circ\text{C}/\text{mm}$ ) and at the growth rate,  $R$ , of 1.2 mm/h. The growth direction is also indicated in Figure 1. The surface of the mixture powder sample (Fig. 1(a)) became smoother as the directional growth process progressed, and a round end was observed at the end of the sample, which indicates that a liquid phase formed in the high-temperature zone, flowed along the pulling direction and

accumulated at the end of the sample. In contrast, the reacted powder sample (Fig. 1(b)) showed a larger width than the mixture powder sample (they had the same width before the directional growth) did, the surface of the reacted powder sample was relatively rough, and a round end was not observed at the end of the sample. The above observations may indicate that the amount of the liquid phase in the mixture powder sample during the directional growth was higher than that in the reacted powder sample.

Figure 2 shows the normalized resistance vs. temperature curves of the samples fabricated using two different precursor powders. Two R-T curves of the directionally grown and the normally sintered samples are included for comparison. The sintered samples were reacted at 950°C for 10 h and annealed at 550°C for 10 h in oxygen flowing atmosphere. The sintered samples showed the critical temperature of about 89 K and tails in the resistance transition range, which indicates that the samples also contain nonsuperconducting impurities. The sample normally sintered using the reacted 123 powder appears to be more impure than that sintered using the mixture powder as shown in the figure, but XRD patterns of the two

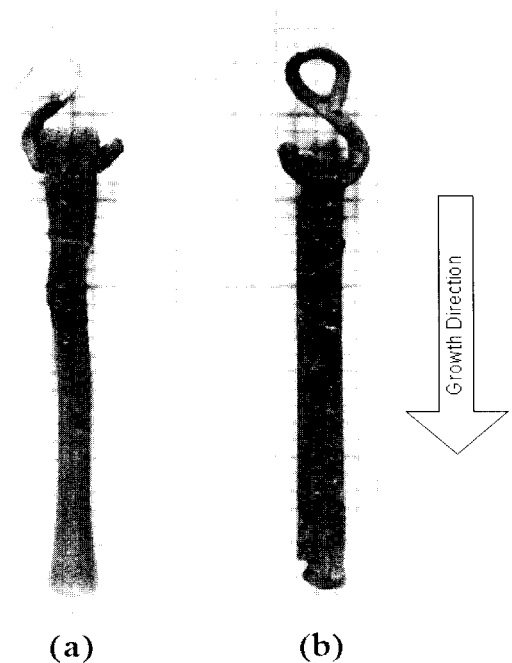


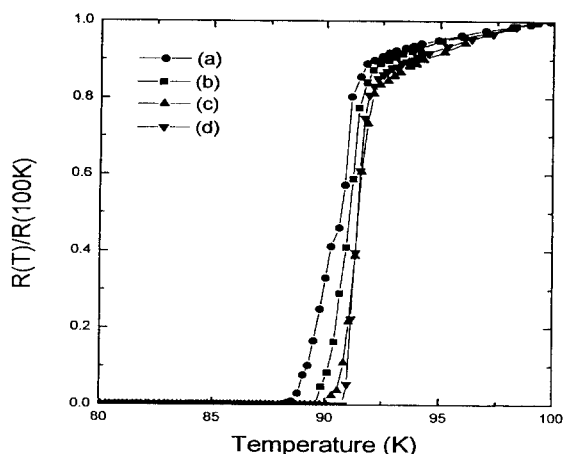
Fig. 1. Appearance of the directionally grown superconductor samples fabricated with (a) 211 + 011 + 001 mixture powder and (b) the reacted 123 powder. Arrow indicates the growth direction, and each square in the figure represents  $1 \times 1 \text{ mm}^2$ .

samples appeared very similar without appearance of any significant impurity phases.

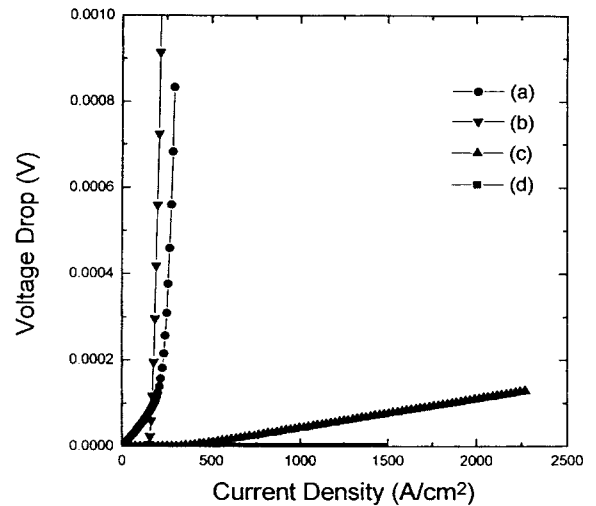
The critical temperature was improved to be over 90 K for the directionally grown samples. It is thought that due to the melting and recrystallization process and the impurity moving along the directional growth, the directionally grown samples always showed higher critical temperature than the sintered samples in this study. The directionally grown sample using the reacted 123 powder shows a tail in the resistance transition range, which indicates that the sample also contains non-superconducting impurities or low temperature superconducting phase. Neither XRD nor SEM analysis revealed detectable any impurity.

Figure 3 shows the voltage vs. current density curves of the samples fabricated using two different precursor powders. The sintered samples showed a critical current density ( $J_c$ ) of about  $200 \text{ A/cm}^2$ , which is a typical value for the sintered 123 superconductors in liquid nitrogen. The directionally grown samples showed improved critical current densities. The sample prepared using a reacted 123 powder showed a  $J_c$  of  $500 \text{ A/cm}^2$ , the sample prepared using a mixture powder showed higher  $J_c$  than can be measured with the instrument used in this study. The current level available in this study was 45 A. Samples extruded using the same precursor powder and directionally grown at the same processing condition showed the  $J_c$  of above  $10^4 \text{ A/cm}^2$  [8].

Figure 4 shows the polarized light images of the microstructures of the polished surface (lengthwise cross-sectional surface) of the



**Fig. 2.** The normalized resistance vs. temperature curves of the following samples: The samples which were fabricated using (a) the reacted 123 powder and (b) the 211+011+001 mixture powder, were sintered at  $950^\circ\text{C}$  for 10 h and annealed at  $550^\circ\text{C}$  for 10 h in oxygen flow. And the samples which were prepared using (c) the reacted 123 powder and (d) the mixture powder, were grown directionally at  $1150^\circ\text{C}$ .

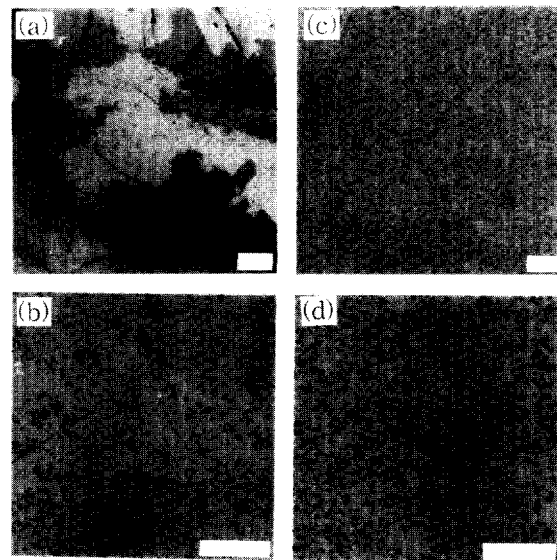


**Fig. 3.** The voltage vs. current density curves of the following samples: (a) The sintered sample with the reacted powder, (b) the sintered sample with the mixture powder, (c) the directionally grown sample with the reacted powder, and (d) the directionally grown sample with the mixture powder.

reacted powder sample (a and b) and the mixture powder sample (c and d) directionally grown at hot-zone temperature of  $1150^\circ\text{C}$  and the pulling speed of  $1.2 \text{ mm/h}$ . The microstructure of the reacted powder sample consisted of hundreds of micron size grains. The grains in the sample consisted of large cracks being parallel inside the grain. These cracks usually perpendicular to the c axis were due to the phase transition of tetragonal phase to orthorhombic phase in 123 lattice. The mixture powder sample showed neither a large angle grain boundary in the whole portion of the microstructure nor a crack, as shown in Fig. 4(c). The sample showed almost void-free microstructure. Trapped particles showing dark contrast were observed in all micrographs and identified as 211 by using EDXS analyses. A ZAF analysis of the EDX spectra collected from the matrix phase showed that the atomic ratio was 1 : 1.9 : 3.1 for Y : Ba : Cu, respectively, which is close to the atomic ratio of 123. The ZAF analysis of the EDX spectra collected from the trapped particle showed that the atomic ratio was 2:0.9:1.2 for Y:Ba:Cu, respectively, which is close to the atomic ratio of 211. In the hot-zone of temperature  $1150^\circ\text{C}$ , the sample consisted of 211 and the peritectic liquid. Just below the peritectic point ( $1015^\circ\text{C}$  [7]), 123 phase crystallized with the trapped 211 particles. The shape and the population density of the trapped 211 particles differed depending on the precursor powder used. The reacted powder sample consisted of needle shape 211 particles, but

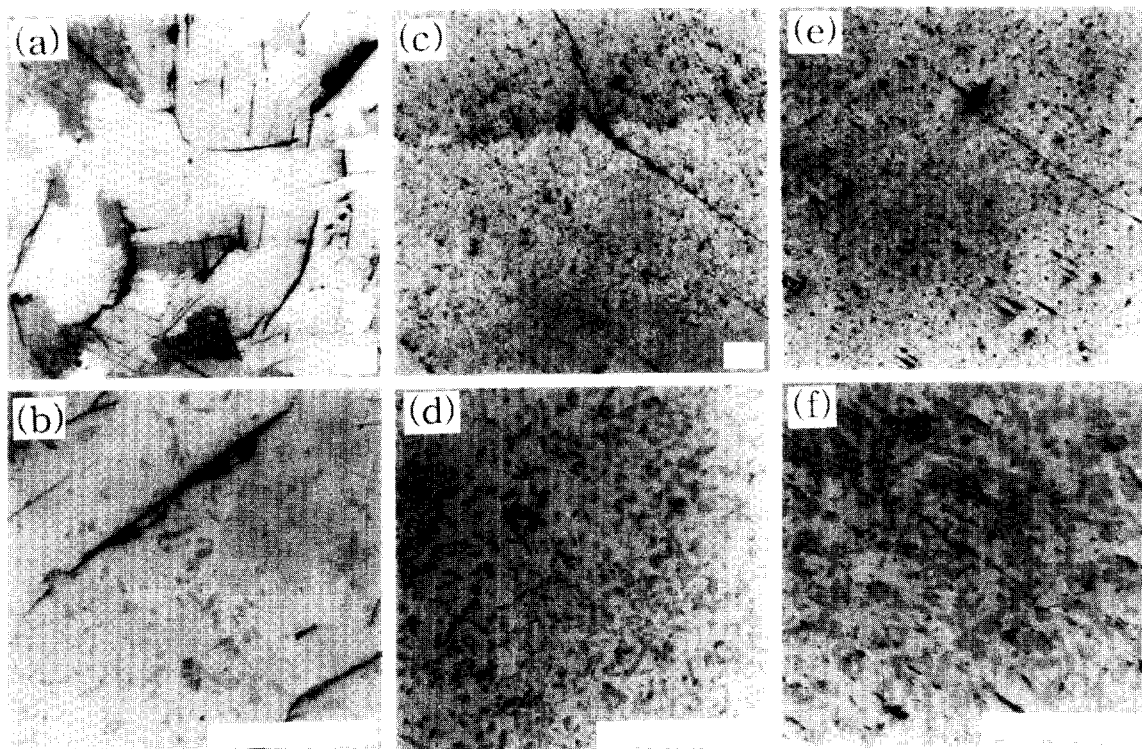
the mixture powder sample consisted of almost equi-axed 211 particles. Similar observations were made in other studies [8~10]. The peritectic decomposition of pure 123 produced acicular prismatic 211 particles, i.e. needle shape in two dimension, while the addition of equiaxed 211 to pure 123 before the decomposition produced equiaxed 211 particles [8]. Acicular 211 particles were obtained for  $Y_2O_3$ -BaCuO<sub>2</sub>-CuO precursor mixture and melt-quenched (MQ) powder, consisting of  $Y_2O_3$ -BaCuO<sub>2</sub> plus amorphous phase, after heated up to 1100°C, while equiaxed 211 particles were obtained for 211-011-001 precursor mixture [9]. Excess 211 in both 123 precursor powder and melt quenched precursor powder produced equiaxed 211 particle after the decomposition at 1100°C [10]. The presence of 211 particles in the precursor powder is important to obtain the equiaxed 211 particles after the decomposition, which is similar situation in this study. The mixture powder sample showed smaller grain size of 211 particle than the reacted powder sample did.

It is well-known that the relationship between 211 particles and  $J_c$  is very close. There is no complete understanding yet as to which of the possible mechanisms contributes to the flux-pinning in the YBCO systems. The smaller 211 particles resulted in higher



**Fig. 4.** Polarized light images of the microstructures of the polished surface (lengthwise cross-sectional surface) of (a and b) reacted powder sample and (c and d) the mixture powder sample directionally grown at hot-zone temperature of 1150°C and the pulling speed of 1.2 mm/h. The white bar represents 100  $\mu$ m.

critical current densities in YBCO system [11]. They used the uniform distribution of very fine 211 particles to enhance the  $J_c$



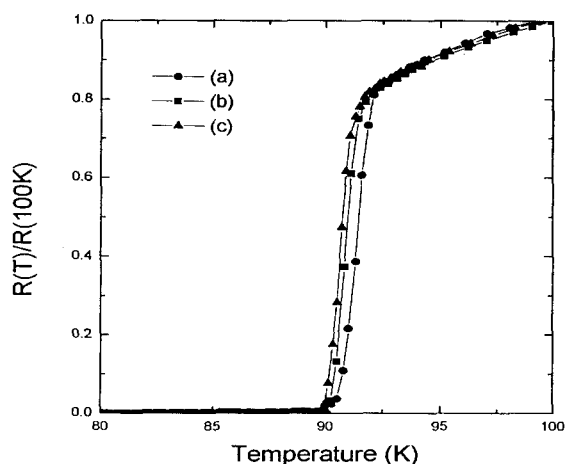
**Fig. 5.** Polarized light images of the microstructures of the polished surface (lengthwise cross-sectional surface) of the reacted 123 powder sample directionally grown at different hot-zone temperatures: (a and b) 1150°C, (c and d) 1175°C and (e and f) 1215°C using the same pulling speed of 1.2 mm/h. The white bar represents 100  $\mu$ m.

drastically, and their results stimulated many other researchers to investigate the effectiveness of the 211 particles as the pinning centers in YBCO system [12-15]. Some speculations are such that the role of 211 particles in the flux-pinning is a secondary effect. In other words, instead of the 211 particles acting as the actual pinning centers, the structural microdefects caused by these 211 particles may be effectively acting as the pinning centers [16-18]. The fine and round 211 particles in the mixture powder sample should be better than the needle shape of the reacted powder sample for the enhancement of  $J_c$ .

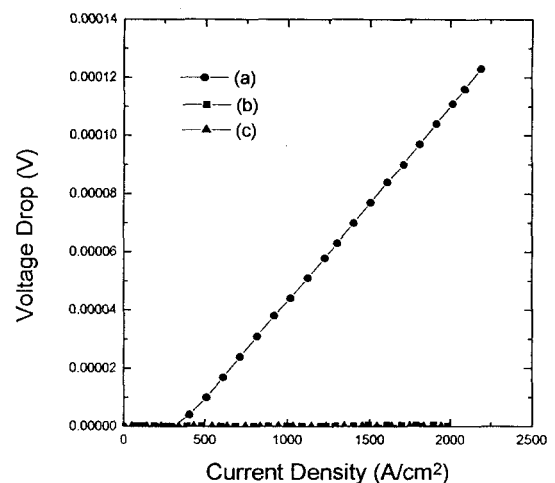
During the directional growth, the reacted powder sample consisted of 123 grains which partially melted to 211 + peritectic liquid above 1015°C. The mixture powder sample consisted of 211, 011 and 001 grains, and these had much large areas for contacts between 211 and 011 grains which form eutectic melt at 1000°C, between 011 and 001 grains which form eutectic melt at 920°C, and between 211 and 011 grains which form peritectic melt at 975°C [7]. The melts formed on the grain contacts formed at lower temperature than the peritectic melt formed on the 123 grains; the amount of the liquid phase in the mixture powder sample would be higher than that in the reacted powder sample; and the directional growth of the mixture powder sample involved a higher amount of melt content, which may improve the texturing. In order to verify the reason that the texturing of microstructure was improved, we grew the reacted powder samples at higher hot-zone temperatures in

which large amount of melt exists.

Figure 5 shows the polarized light images of the microstructures of the polished surface (lengthwise cross-sectional surface) of the reacted 123 powder samples directionally grown at different temperatures using the same pulling speed of 1.2 mm/h. The microstructures of the reacted powder sample were investigated with different temperatures : 1150°C (Fig. 5(a), (b)), 1175°C (Fig. 5(c), (d)), and 1215°C (Fig. 5(e), (f)). As the hot zone temperature increased, the number of the grains decreased in the same range of the microstructures, and the sample grown directionally at 1215°C ( $G=15^\circ\text{C}/\text{mm}$ ) appears to consist of a single grain without a large angle grain boundary in the whole range of the microstructure. All microstructures of three samples showed voids and cracks being parallel to each other. But the microstructures of the mixture powder samples are almost crack- and void-free as shown in Fig. 4(c). The shape of the trapped 211 particles was not changed as the acicular shape at the hot zone temperature. The results may indicate that the quality of the sample is better for the mixture powder sample than for the reacted powder sample. The volume fraction of 211 particle for the three samples grown at 1150°C, 1175°C and 1215°C were estimated by using a computer image analysis. The 211 volume fraction of three samples grown at 1150°C, 1175°C, and 1215°C were about 11%, 26%, and 36%, respectively. As one considers the YBCO phase diagram and the equation mentioned below, with increasing the hot-zone temperature, the amount of liquid increased and the viscosity

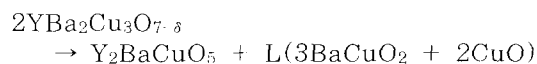


**Fig. 6.** Normalized resistance vs. hot-zone temperature curves of the samples fabricated with the reacted 123 powder and directionally grown at (a) 1150°C, (b) 1175°C, and (c) 1215°C with the same pulling speed of 1.2 mm/h.



**Fig. 7.** Voltage vs. the current density curves of the samples fabricated with the reacted 123 powder and directionally grown at (a) 1150°C, (b) 1175°C, and (c) 1215°C with the same pulling rate of 1.2 mm/h.

of liquid of the samples decreased.



As shown in Fig. 5(d) and (f), the size and volume fraction of 211 particles in the sample grown at 1215°C (Fig. 5(f)) were larger than that in the sample grown at 1175°C (Fig. 5(d)). It is known that the growth rate of the solid grain in liquid increases exponentially with increasing temperature. Therefore the higher the temperature of hot zone is, the larger the size of 211 particle in the grown sample is. In a partially molten state, the volume fraction of 211 particle at 1215°C is lower than at 1175°C according to YBCO phase diagram. This is contrary to the present results observed. It can be explained as follows: As the hot-zone temperature increases, the viscosity of liquid is likely to decrease. Therefore on pulling the sample, the liquid of hot-zone at a relatively high temperature (1215°C) is easier to flow downward than that with a relatively low temperature (1175°C).

Figure 6 shows the normalized resistance vs. hot-zone temperature curves for the reacted 123 powder samples directionally grown at different hot-zone temperatures with the same pulling speed of 1.2 mm/h. All the samples show sharp transition within a similar narrow temperature range. As the hot-zone temperature increased, the curve of transition showed shorter tails. But the critical temperatures slightly decreased with increasing the hot-zone temperature. The curves of two samples grown at 1150°C and 1175°C had tails during the transition. It suggests that those samples might have some of phases. Figure 7 shows the voltage vs. the current density curves of the reacted 123 powder samples directionally grown at different hot-zone temperatures but with the same pulling rate. As the hot-zone temperature increased, i. e. the temperature gradient increased, the  $J_c$  increased, and the slope of the curve above the  $J_c$  decreased. The sample grown directionally at 1215°C showed the  $J_c$  above the limitation of the current source (45 A) available for the present study. These observations are consistent with the results shown in Fig. 5, in which the texturing improved as the hot-zone temperature increased. Therefore, in microstructures and superconducting properties, the sample grown at 1215°C showed the best quality of them. Although the sample showed the best result among them, the sample still had cracks and large 211 particle.

When the sample grown with the reacted powder at 1215°C was compared with the

mixture powder sample grown at 1150°C, the latter was better in size and shape of the 211 particle and cracks than former. The microstructures and the superconductivities of the superconductors grown directionally were rather influenced by the difference of precursors than by the amount of melt in the samples.

#### 4. Summary

Textured bulk  $\text{YBa}_2\text{Cu}_3\text{O}_x$  superconductor samples were fabricated using directional growth of superconductor grains reacted from both reacted  $\text{YBa}_2\text{Cu}_3\text{O}_x$  powders, and  $\text{Y}_2\text{BaCuO}_5$ ,  $\text{BaCuO}_2$  and  $\text{CuO}$  mixture powder. The microstructure and superconducting properties of the samples were compared. The mixture powder sample showed a better microstructure (dense, crack-free) and higher  $J_c$ . The shape of the 211 inclusions was equiaxed for the mixture powder sample but needle shaped for the reacted powder sample, and the population density of the inclusion in the mixture powder sample was higher than that of the reacted powder sample. As the hot-zone temperature increased, the texturing of the reacted powder sample was improved, and the  $J_c$  increased. The microstructure of the mixture powder sample grown directionally at hot-zone temperature of 1150°C was better than that of the reacted powder sample grown directionally at 1215°C. The better microstructure and the superconducting properties of the mixture powder sample than those of the reacted powder sample at the same directional growth condition may be rather influenced by the kind of precursors than by the amount of melt in the samples.

#### References

- [1] M. Murakami, Melt Processed High Temperature Superconductors, (World Scientific Publishing Co, 1992) p 21-67.
- [2] K. No, D. Yoon, W.S. Shin, W. Kim and G. Shim, J. Mater. Sci. 29 (1994) 2345.
- [3] W. Kim, D. Jang, C. Suh, K. No and W. Shin, Jpn. J. Appl. Phys. 33 (1994) 999.
- [4] K. No and W. Shin, J. Mater. Sci. 30 (1994) 3183.
- [5] S. Jin, T.H. Tiefel, R.C. Sherwood, R.B. Van Dover, M.E. Davis, G.W. Kammlott, and R.A. Fastnacht, Phys. Rev. B 37 (1988) 7850.
- [6] K. No, D.S. Chung, J.M. Kim, H.Y. Kim and G. Shim, J. Mater. Sci. 26 (1991) 3593.
- [7] T. Aselage and K. Keefer, J. Mater. Res. 3 (1988) 1280.

- [8] M. L. Griffith, R. T. Huffman and J. W. Halloran, *J. Mater. Res.* 9 (1994) 1633.
- [9] N. Sakai, S. I. Yoo and M. Murakami, *J. Mater. Res.* 10 (1995) 1611.
- [10] F. Frangi, T. Higuchi, M. Deguchi and M. Murakami, *J. Mater. Res.* 10 (1995) 2241.
- [11] H. Fujimoto, M. Murakami, S. Gotoh, N. Koshizuka, and S. Tanaka, *Adv. Supercond.* 2, (1990) 285.
- [12] D.F. Lee, X. Chaud, and K. Salama, *Jpn. J. Appl. Phys.* 31, (1992) 2411.
- [13] M. Wacenovskiy, R. Miletich, H.W. Weber, and M. Murakami, *Supercond. Sci. Technol.* 4, (1991) S184.
- [14] S. Gotoh, N. Koshizuka, M. Yoshida, M. Murakami, H. Fujimoto, and S. Tanaka, *Supercond. Sci. Technol.* 4, (1991) S226.
- [15] E.H. Lee, S.H. Oh and S.Y. Yoon, *Jpn. J. Appl. Phys.* 31, (1992) 1318.
- [16] M. Murakami, S. Gotoh, H. Fujimoto, K. Yayaguchi, N. Koshizuka, and S. Tanaka, *Supercond. Sci. Technol.* 4, (1991) S43.
- [17] Z.L. Wang, A. Goyal, and D.M. Kroeger, *Phys. Rev. B* 47 (1993) 5373.
- [18] T.H. Sung, M.J. Cima, M.C. Flemings, J.S. Haggerty, S. Honjo, K. Rigby, H. Shen, and J.D. Yoo, *Tenth Quarterly Report Mater. Proc. Center, M.I.T.* Nov. (1994).



**이준성(李峻誠)**

1972년 2월 14일 생, 1995년 포항공과대학교 물리학과 졸업, 1997년 동 대학원 물리학과 졸업(이학석사), 현재 한국전력공사 전력연구원 근무.



**김유진(金裕進)**

1974년 1월 5일생, 1998년 한양대학교 무기재료공학과 졸업, 현재 한국과학기술원 재료공학과 석사과정.



**노광수(盧光洙)**

1955년 2월 5일생, 1977년 한양대학교 요업공학과 졸업, 1979년 서울대학교 요업공학과 졸업, 1986년 Iowa 주립대학교 재료공학과 졸업, 1986-88년 미국 에너지성 Ames Laboratory Post. Doc., 현재 한국과학기술원 재료공학과 교수.

**저자 소개**



**성태현(成台鉉)**

1959년 10월 9일 생, 1982년 한양대학교 공대 무기재료공학과 졸업, 1987년 동 대학원 무기재료공학과 졸업(공학석사), 1991년 동경공업대학 재료과학 전공(공학박사), 1991 - 1992년 ISTEK 근무, 1992 - 1995년 MIT Post. Doc., 현재 한국전력공사 전력연구원 근무.



**한상철(韓相哲)**

1966년 3월 26일 생, 1987년 고려대학교 공대 금속공학과 졸업, 1990년 KAIST 재료공학과 졸업(공학석사), 1995년 KAIST 재료공학과 졸업(공학박사), 현재 한국전력공사 전력연구원 근무.



**한영희(韓榮熙)**

1965년 8월 1일 생, 1988년 서울대학교 공대 무기재료학과 졸업, 1990년 동 대학원 무기재료학과 졸업(공학석사), 현재 한국전력공사 전력연구원 근무.