Direct fabrication of a large grain YBCO bulk superconductor without intermediate grinding step

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Abstract

Large grain YBCO bulk superconductors are fabricated by the top-seeded melt growth (TSMG) or top-seeded infiltration growth (TSIG) method. Both growth methods use at least one of $YBa_2Cu_3O_{7-\delta}$, Y_2BaCuO_5, $BaCuO_3$ pre-reacted precursor powders. However, the synthesis of the pre-reacted powders includes multiple calcination runs which are cost-bearing and time-consuming. In this work, we report the successful growth of single-domain YBCO bulk superconductors directly by using the powder compact that has been pressed from the mixture of Y_2O_3, $BaCO_3$ and CuO powders without any intermediate grinding step. Single-domain YBCO bulk superconductor has been also prepared by using Y_2O_3, BaO_2 and CuO powders without intermediate grinding step. Investigations on the trapped magnetic field and microstructure of the melt-processed specimen show that the elimination of the repeated processes of calcinations and pulverization has hardly affected on the crystal growth and the magnetic properties of the grown YBCO bulk superconductors. However, it is thought that the presence of residual carbon affects on the size of Y211 particles in melt-processed YBCO bulk superconductor.

Keywords: REBCO, bulk superconductors, Y211, starting precursor

1. INTRODUCTION

Single grain $REBa_2Cu_3O_{7-y}$ (RE123, RE: rare-earth elements) bulk superconductors have a great potential for the applications of magnetically-levitated system, permanent magnets, magnetic shielding, and so on [1, 2]. The large grain YBCO bulk superconductors have been fabricated by a top-seeded melt growth (TSMG) or by a top-seeded infiltration growth (TSIG) process [3-8]. Both of TSMG and TSIG is consisted of various steps of the mixing of starting precursor powders, calcination, grinding, compaction, high temperature anneal for melt formation, slow cooling for crystal growth and low temperature anneal for oxygenation. Y_2O_3, $BaCO_3$ and CuO powders have been used as starting powders and Y123, $BaCuO_3$ and Y211 powders have been prepared by the calcination heat treatment. The combined process of calcination heat treatment and mechanical grinding is repeated three times in general for the complete decomposition of $BaCO_3$ starting precursor.

Extra time and cost arise by the repeated heat treatment and mechanical grinding. Therefore, there have been attempts to simplify the repeated process [9, 10]. Recently, $BaCO_3$ carbonate precursor has been replaced into BaO_2 oxide powder [9]. BaO_2 precursor contains no carbon and therefore single time calcination was enough for the preparation of a single grain REBCO bulk superconductor with high magnetization characteristics. High magnetization single grain GdBCO bulk superconductor

has been also fabricated directly by using the powder compact which has been prepared using Gd_2O_3, BaO and CuO powders without any intermediate grinding step [10]. Even though the synthesis procedure of the pre-reacted powders steps has been simplified, there is another big drawback of high price of BaO or BaO_2 powder compared to $BaCO_3$ powder. Therefore, it is desirable if we can simplify the preparation procedure of the powder compact with the use of cost-effective $BaCO_3$ precursor as a barium source.

In this article, it is presented that the single grain REBCO bulk superconductors have been prepared directly by using $BaCO_3$ precursor as a barium precursor and by eliminating the grinding step in TSMG method. The microstructure and the magnetic property of the melt-processed specimen are discussed.

2. EXPERIMENTALS

Three different precursor powders were prepared by using high purity powders of Y_2O_3, BaO_2, $BaCO_3$, CuO and CeO_2. Nominal composition of the precursor was Y:Ba:Cu = 1.8: 2.4: 3.4 and 1 wt. % CeO_2 was added as a refiner of Y211 particles. Pre-reacted precursor powder mixture (purchased from Superconductor Components Inc.), which has been synthesized by repeated calcinations and grinding procedure, was mixed with 1 wt. % CeO_2 (hereafter, Y1.8-SCI). Additionally, two different kinds of powder mixture were also prepared by mixing Y_2O_3, BaO_2 (or

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BaCO$_3$), CuO and CeO$_2$ powders. BaO$_2$ powder (hereafter, Y1.8-oxide) and BaCO$_3$ powder (hereafter, Y1.8-carbonate) are used as Ba source, respectively. The nominal composition of both Y1.8-oxide and Y1.8-carbonate is the same with Y1.8-SCI.

An appropriate amount of Y1.8 powder was put into a steel mold with a diameter of 25 mm. Compacts were prepared by a uni-axial pressing and then cold isostatic pressed. Y1.8-oxide compact and Y1.8-carbonate compact were sintered at 950℃ for 24h in air. Extra Y1.8-carbonate compacts with a diameter of 40 mm were prepared in order to investigate the effects of the compact dimension on the calcinations. Extra Y1.8-carbonate compacts were heat treated at 800℃ for 8h, 850℃ for 8h, 900℃ for 8h and 950℃ for 8h in air.

For TSMG, powder compact was placed on the Yb$_2$O$_3$ pieces and then a small-sized Sm-123 seed was put on the top surface of the Y1.8-SCI pellet at last. For Y1.8-oxide and Y1.8-carbonate, sized Sm-123 seed was put on the top surface of the calcined pellet. The heat treatment procedure for melt growth (MG) was similar to those reported in the literature [15]. The cooling rate controlled with 0.4℃h^{-1} at the temperature regime for the growth of Y123 grains. After the MG heat treatment, Y1.8 samples were heated to 500℃ at a rate of 200℃h^{-1} in flowing oxygen for oxygenation, held at this temperature for 50 h, cooled to 400–500℃ at a rate of 100℃h^{-1}, held at this temperature for 200-300 h, and then cooled to room temperature at a rate of 200℃h^{-1}.

Trapped magnetic fields at 77 K were measured for the slab surface and the cross section of the field-cooled samples. A trapped magnetic field (B) measurement was performed on field-cooled samples. Permanent magnet with a diameter of 30 mm and a surface field of 4.9 kG was placed on the sample, and liquid nitrogen was poured thereon to cool the sample to 77K (field cooling, FC). When the temperature of the sample reached 77 K, the permanent magnets placed on the superconductor were removed, and the magnetic force trapped in the superconductor was measured on the top surface using a hall probe. The microstructures of the melt-processed specimen were also investigated using optical microscope (OP).

3. RESULTS AND DISCUSSION

Fig. 1 shows the trapped magnetic field of the specimens that the powder compact has been prepared by using the pre-reacted powders (Y1.8-SCI) and the raw materials of Y$_2$O$_3$, BaO$_2$ and CuO powders (Y1.8-oxide), respectively. There is no significant difference in the trapped magnetic field with a single peak at the center of the specimen. Therefore, it is thought that the use of pre-reacted powders is not a pre-requisite for the fabrication of high magnetization REBCO bulk superconductors. Nearly symmetric contour lines of magnetic field also show that the specimen is consisted of a large single grain. Wang et al. [10] has already reported that a single grain GdBCO bulk
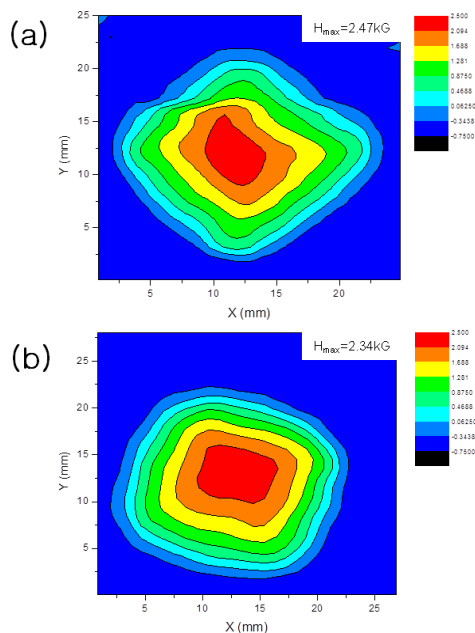

Fig. 1. Trapped magnetic field of the specimens that the powder compact for MG have been prepared by using (a) the pre-reacted powders and (b) the raw material powders, respectively.

superconductor has been fabricated by using the powder compact which was directly formed using Gd$_2$O$_3$, BaO, CuO and CeO$_2$ powders instead of using the pre-reacted powders of Gd123 and Gd211. In other words, they have eliminated the multiple heat treatment steps for the synthesis of Gd123 and Gd211 powders. More previously, Li et al. [9] has reported that a high quality YBCO bulk superconductor has obtained by using Y$_2$O$_3$, BaO$_2$, CuO and CeO$_2$ powders with single step calcination heat treatment. It means that single step calcination is enough for the fabrication of high magnetization YBCO bulk superconductor when BaCO$_3$ has been substituted into BaO$_2$ powder as a Ba source.

Fig. 2 shows the high magnification optical microstructures of the melt processed Y1.8-oxide specimen. It is seen that Y211 particles are finely dispersed. The size of Y211 particles is much smaller in the middle of the specimen than Y211 particles at about 1-mm beneath at the top surface. The size of Y211 is estimated as of about 1~2 μm and the morphology of Y211 is nearly round shape. It has been reported that the sub-micron size Y211 particle has obtained by the high energy ball milling process for the melt-processed REBCO bulk superconductors [11, 12]. On the other hands, it has been reported that the infiltration growth (IG) method has lead to the formation of sub-micron size Y211 particle [13, 14]. The size of Y211 is strongly dependent on the size of the starting powders in IG method [14]. Sub-micron sized Y211 has been formed during the IG process when the sub-micron Y$_2$O$_3$ powder is used in the solid source pellet [13]. The morphology of the Y211 particle shows mostly round shape in the specimen prepared by the IG method that is similar to the results of this work. It is not clear yet why small round-shaped Y211 particles have been formed in Y1.8-oxide specimen.
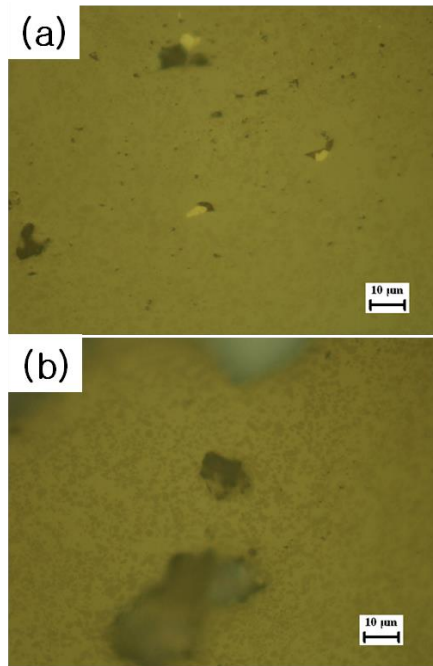
Fig. 2. High magnification optical microstructures of the melt-processed Y1.8-oxide specimen. (a) close to the top surface and (b) at the center of the specimen, respectively.
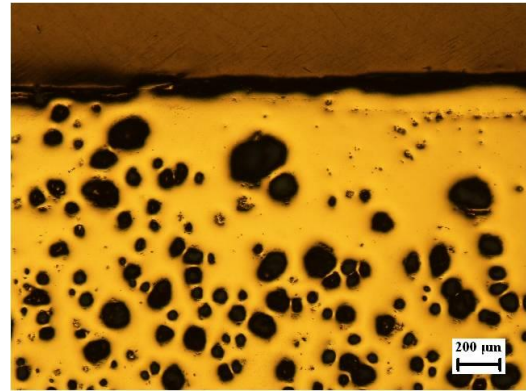

Fig. 3. Low magnification optical cross-sectional microstructure of the melt-processed Y1.8-oxide specimen close to the top surface.
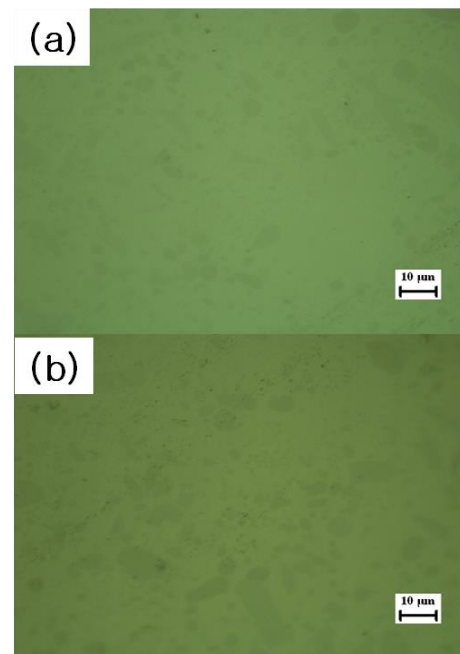

Fig. 4. High magnification optical microstructures of the melt-processed Y1.8-SCI specimen. (a) close to the top surface and (b) at the center of the specimen, respectively.

Fig. 3 shows a low magnification optical microstructure of the Y1.8-oxide specimen. It is seen that large number of pores are present even near to the top surface. The size of Y211 particles is much finer compared to the size of Y211 particles of the Y1.8-SCI specimen as appeared in Fig. 4. It is also seen that the density of Y211 particle is lower for Y1.8-SCI specimen than for the Y1.8-oxide specimen. It has been known that the size and the molar fraction of Y123 and Y211 affects on the growth behavior of Y123 crystal and the magnetic properties of the melt-processed YBCO bulk superconductor [15, 16]. It may be reasonable to expect better magnetic properties in the Y1.8-oxide specimen than in the Y-1.8-SCI because the size of Y211 is much finer. However, there is a small difference between the trapped magnetic fields of two specimens. Therefore, it is thought that the relatively low trapped magnetic field of the Y1.8-oxide specimen may be due to the existence of the large number of pores through the whole specimen. From the observations of the microstructures and the magnetic properties of the Y1.8-oxide specimen and the Y1.8-SCI specimen, it is thought that the use of BaO or BaO_2 powder is one of the ways to simplify the fabrication process of a high magnetization REBCO bulk superconductors as already reported previously [9, 10]. However, the price of barium oxide is much expensive compared to the price of barium carbonate.

In the conventional melt growth methods, repeated calcination heat treatments have been carried out with intermediate grinding steps in order to complete conversion of precursor powders into Y123 and Y211 powders through the conversion reactions of $1/2Y_2O_3 + 2BaCO_3 + 3CuO \rightarrow Y123$ and $Y_2O_3 + BaCO_3 + CuO \rightarrow Y211$. It has been reported that the residual carbon content higher than 500 ppm largely depresses the superconducting transition

temperature [17]. Repeated calcinations runs have reduced the residual carbon content continuously in the pre-reacted powders after calcinations as well as in the melt-processed specimen with the number of run.

Fig. 5 shows the digital images of the Y1.8-carbonate specimen after the calcinations run that barium carbonate has been used for the preparation of the powder compact for TSMG process. Four different specimens have been prepared: two tall specimens with and without CIP and two thin slabs with and without CIP. Calcination has been conducted via the consecutive heat treatments at 800℃ for 8h, 850℃ for 8h, 900℃ for 8h and 950℃ for 8h in air. It is seen that multiple lateral cracks are visible for the YBCO compact without CIP step irrespective of the thickness of the compact. However, macroscopic cracks are largely decreased for the CIPed specimen although relatively small size cracks are present yet. It is noticeable that there is a
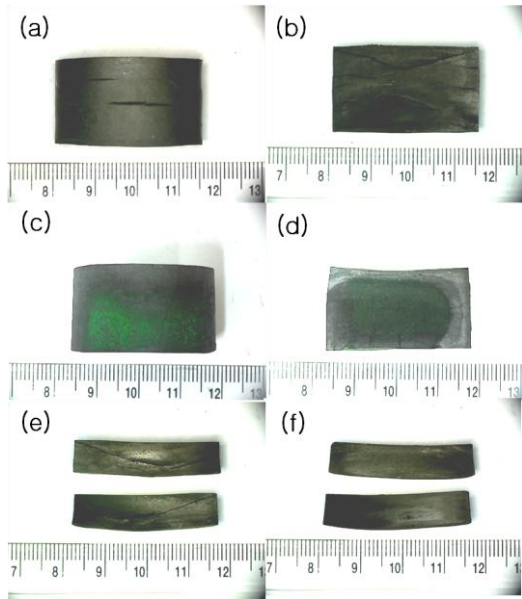
Fig. 5. Digital images of the sintered specimens of Y1.8-carbonate. Side view (a) and cross sectional view (b) of the tall specimen prepared by a uni-axial pressing, respectively. Side view (c) and cross sectional view (d) of the tall specimen prepared by a cold isostatic pressing, respectively. (e) Cross sectional view the thin slab prepared by a uni-axial pressing. (f) Cross sectional view the thin slab prepared by a cold isostatic pressing.

shape deformation of YBCO compact after the calcinations step. It is also observed that non-uniform structure is developed for the CIPed compact. Structure non-uniformity is thought to be closely related to the formation of the melt phase. It is seen that the cracks are observed at the peripheral crust of the CIPed compact. Therefore, it seems that the cracks are formed during the cooling stage.

As shown in Fig. 5, CIP has largely suppressed the formation of macro-cracks which might be detrimental for the fabrication of a quality REBCO bulk crystal. However, CIP had resulted in the structural non-uniformity. Therefore, relatively small sized compacts have been prepared using a steel mold with a cavity diameter of 25-mm in order to reduce the effects of the structural non-uniformity on the growth of Y123 grain.

Fig. 6 shows the digital images of the Y1.8-carbonate specimen prepared by a top-seeded melt growth method. It is seen that the specimen is consisted of a single grain with an x-shaped facet lines. However, the x-shaped facet lines are not prominent because the specimen surface is not reflective due to the rough surfaces. Side view picture shows a <110> facet line which is also one of the clues of the single grain growth in melt-processed REBCO bulk specimen.

Fig. 7 shows the high magnification optical microstructures of the melt processed Y1.8-carbonate specimen. The size of Y211 particles of the melt processed Y1.8-carbonate specimen is relatively large compared to that of the melt processed Y1.8-oxide specimen. It is rather comparable with that of the melt processed Y1.8-SCI
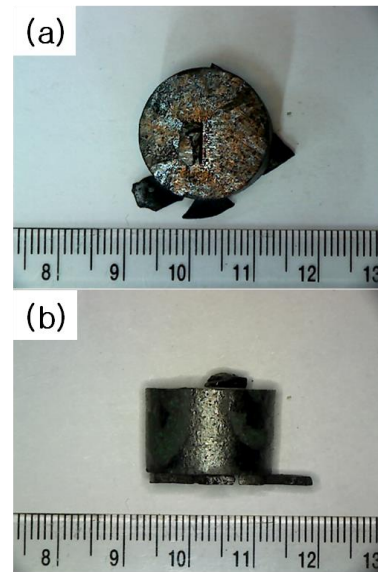

Fig. 6. Digital images of the Y1.8-carbonate specimen prepared by a top-seeded melt growth method. (a) top-view and (b) side-view. Calcination heat treatment has been made at 950℃ for 24h in air.

specimen. It is evident that both of Y1.8-SCI and Y1.8-carbonate have been prepared by using barium carbonate as a raw material of barium source. Even though the repeated number of calcination runs, the residual carbon has been remained [18]. Therefore, it can be though that the formation of fine Y211 particle in melt-processed Y1.8-oxide specimen might be due to the little carbon content compared to Y1.8-SCI and Y1.8-carbonate.

Fig. 8 shows the trapped magnetic field of the Y1.8-carbonate specimen. It is seen that the trapped magnetic field of the Y1.8-carbonate specimen is not much different from those of both Y1.8-SCI specimen and the Y1.8-oxide specimen. Sofie and Dogan [18] has reported that the residual carbon has decreased the superconducting transition temperature (Tc) and the critical current density (Jc) under zero magnetic field at 77k. However, Jc was increased under a high magnetic field with the carbon content due to a fish-tail effect. Therefore, further works are needed in order to know the factors which have affected on the trapped magnetic field in Y1.8-carbonate.

4. CONCLUSIONS

Three different types of precursor powders have been used for the fabrication of a large-grain YBCO bulk superconductor by a top-seeded melt growth method. Y1.8-oxide and Y1.8-carbonate specimen have eliminated the mechanical grinding step for precursor preparation procedure. All specimens have showed comparable magnetization characteristics even though simplified processing procedure has been used for the fabrication of oxide-Y1.8 and carbonate-Y1.8 specimen. It is suggested that the elimination of residual carbon in the specimen might be one of the important factors for the refinement of Y211 particles.
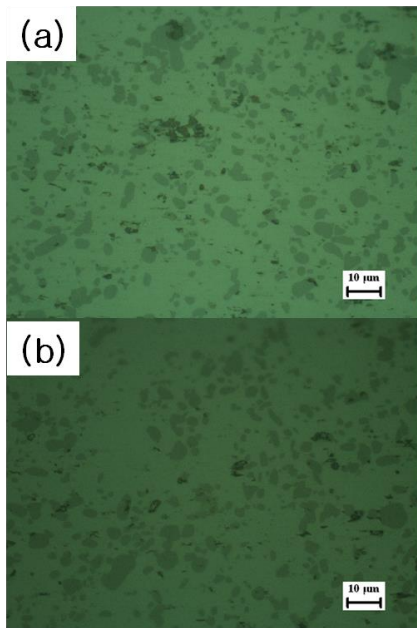
Fig. 7. High magnification optical microstructures of the melt processed Y1.8-carbonate specimen.
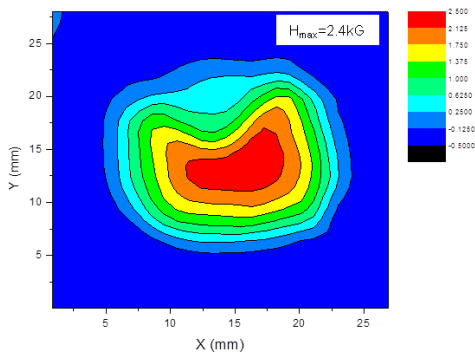

Fig. 8. Trapped magnetic field of the melt-processed Y1.8-carbonate. Calcination heat treatment has been made at 950℃ for 24h in air.

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