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Fabrication of Bi2223 bulks with high critical current properties sintered in Ag tubes

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ABSTRACT

Randomly grain oriented Bi2223 sintered bulks are one of the representative superconducting materials having weak-link problem due to very short coherence length particularly along the *c*-axis, resulting in poor intergrain J_c properties. In our previous studies, sintering and/or post-annealing under moderately reducing atmospheres were found to be effective for improving grain coupling in Bi2223 sintered bulks. Further optimizations of the synthesis process for Bi2223 sintered bulks were attempted in the present study to enhance their intergrain J_c. Effects of applied pressure of uniaxial pressing and sintering conditions on microstructure and superconducting properties have been systematically investigated. The best sample showed intergrain J_c of 2.0 kA cm^{-2} at 77 K and 8.2 kA cm^{-2} at 20 K, while its relative density was low ~65%. These values are quite high as for a randomly oriented sintered bulk of cuprate superconductors.

1. Introduction

$(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (Bi2223) is one of the most promising cuprate superconductors in various application fields. In a recent decade, the critical current [I_c] of commercial Ag-sheathed Bi2223 tapes with a typical cross-section area of 1 mm^2 has been largely improved up to 200 A at 77 K in self-field [1], which corresponds to a critical current density J_c of $\sim 6 \times 10^4$ A cm^{-2} at the superconducting Bi2223 filaments. Introduction of the controlled-over-pressure (CT-OP) method [2] with careful control of oxygen partial pressure P_{O2} has been a key technology to lead to the improved critical current performance suitable for various applications, such as superconducting transmission cables [3], superconducting coils for high resolution NMR [4], motors [5], induction heaters etc.

History of Ag-sheathed Bi2223 tapes has started [6–9] just after the discovery of Pb-doping effect on promoting the phase formation of Bi2223 [10, 11]. Since the Bi2223 has a layered crystal structure along the *c*-axis with thick blocking layer, Bi2223 crystals have thin plate-like shape with wide *ab*-plane, which is parallel to the superconducting CuO_2 plane, and J_c in the *ab*-plane is much higher than that in the *c*-axis direction. Therefore, *c*-axis orientation is crucially important to synthesis of the polycrystalline materials with high critical current density. In the synthesis procedures of Bi2223 tapes, uniaxial pressing and flat rolling after formation of Bi2223 phase were well known to be quite effective for fabrication of *c*-axis oriented Bi2223 filaments. The above mentioned CT-OP method applied for rolled tapes after first sintering mainly improves density and homogeneity of Bi2223 filaments.

On the other hand, development of Bi2223 sintered bulk materials has been less active particularly since late 1990s mainly due to their quite low J_c compared to the Ag-sheathed tapes. Typical intergrain J_c values at 77 K of the randomly grain oriented Bi2223 bulk sample was low ~200 A cm^{-2} [12] due to the weak grain coupling originated in short coherence length and porous microstructure with poor grain connecting area. Even for *c*-axis aligned bulks and highly dense bulks, which are fabricated by introduction of intermediate uniaxial pressing process [13–15] and by over-pressure sintering process using hot isostatic pressing (HIP) apparatuses [16, 17], respectively, the intergrain J_c values remained below ~ 1 kA cm^{-2}. At the present stage, Bi2223 sintered bulk materials are used only for superconducting current leads of superconducting magnet systems cooled by cryocoolers, because this application requires low thermal conductivity and I_c ~200 A at 77 K at cross section larger than 1 cm^2. J_c of the cylindrical bulk current leads prepared by repetition of cold isostatic pressing (CIP) process and

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sintering was reported to be 842 A cm^{-2} at 77 K [18], whereas they have dense and partially c-axis oriented microstructure.

In our previous studies, the critical temperature [T_c] of Bi2223 practical tapes was found to be enhanced up to 115 K by post-annealing at ~700 °C in air for a long time [19]. This annealing process changes nonstoichiometric cation compositions, while it accompanies deterioration of grain coupling by generation of non-superconducting $(Pb,Bi)_3Sr_2Ca_2CuO_y$ [Pb3221] precipitates [19, 20]. Since the lead ions are tetravalent in Pb3221, this phase does not generate when the post-annealing is carried out under moderately reducing atmosphere. By optimization of post-annealing conditions, Bi2223 tapes with high T_c above 115 K were successfully prepared without degrading the grain coupling [21]. In addition, the reductive post-annealing process is also effective for improving the grain coupling of Bi2223 polycrystalline bulks [22]. On the other hand, recent our studies revealed that first sintering under slightly reducing atmospheres of $P_{O2} < 5$ kPa promotes the phase formation of Bi2223, resulting in highly pure Bi2223 samples even by a short time sintering less than 10 h [23]. Such short time sintering is favorable for suppression of grain growth of impurity phases.

Since these new heat-treatment procedures are considered to be effective for improving J_c of Bi2223 sintered bulks, we have attempted to optimize the fabrication conditions of the Bi2223 bulks in terms of high critical current properties in the present study. Furthermore, we have re-examined the fabricating processes, such as pressure of the uniaxial pressing and sintering in sealed Ag tubes to suppress vaporization of bismuth and lead at high temperatures.

2. Experimental

The nominal molar ratio of the Bi2223 sample was Bi: Pb: Sr: Ca: Cu ~ 1.7: 0.35: 1.9: 2.0: 3.0. The calcined powder obtained by heating at 780 °C for 6 h in air was composed of $(Bi,Pb)_2Sr_2CaCu_2O_y$ [Bi2212] as the main phase. The powder was filled into Ag tubes (3 mmϕ / 4 mmϕ) and they were uniaxially pressed into a thick tape shape under pressures P_1 of 50–300 MPa and both ends were sealed by pressing. The first-sintering to form the Bi2223 phase was performed at 815–825 °C for 6–18 h under $P_{O2} = 3$ kPa by flowing 3% O_2/Ar. After the first-sintering, the samples were uniaxially pressed again under pressures P_2 of 50–300 MPa for densification of the oxide layer. Since the thickness of the sample is ~1 mm, the c-axis grain alignment by uniaxial pressing occurred only at the interface between silver and oxide layers. The second sintering to recover grain coupling deteriorated by pressing was done at 825 °C for 6 h under $P_{O2} = 3$ kPa. In each sintering, samples were slowly cooled down to 20 °C below the sintering temperature for 3 h. Some bulks were post-annealed at 740 °C for 100 h under $P_{O2} = 500$ Pa in order to control nonstoichiometric cation compositions. Oxygen annealing at 350 °C for 6 h was performed for some samples to increase the oxygen content of Bi2223 for achieving the carrier over-doped state.

Constituent phases were analyzed by X-ray diffraction (XRD). The microstructure was examined by scanning electron microscopy (SEM). Superconducting properties were evaluated by magnetization measurements using a SQUID magnetometer (Quantum Design, MPMS) and resistivity measurements were performed by conventional four-probe method by applying ac current using a Physical Property Measurement System (Quantum Design). Inter-grain J_c, $J_{c\,(intergrain)}$, was examined by remanent magnetization measurements. In the magnetization measurements, magnetic fields were always applied vertical to the wide surface of samples, *i.e.*, parallel to the uniaxial pressing direction.

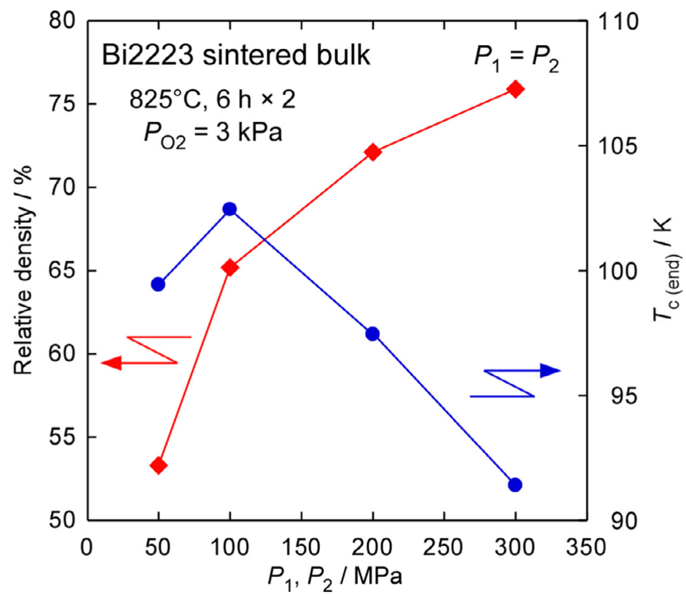

Fig. 1. Dependence of relative density and $T_{c\,(end)}$ defined as electrical resistivity $\rho = 1\,\mu\Omega$ cm of Bi2223 sintered bulks on applied pressure of uniaxial pressing.

3. Results and discussion

3.1. Optimizing pressure of the uniaxial pressing

Uniaxial pressing is known to be an effective technique to prepare highly dense and c-axis oriented bulks. However, optimization of uniaxial pressure is quite important, because extremely high pressure may result in unrecovered cracks and/or largely deformed crystals. In order to determine the optimal uniaxial pressing conditions, effects of pressures of the uniaxial pressing P_1 and P_2 on relative density and superconducting properties were systematically examined. Bi2223 sintered bulks uniaxially pressed under $P_1 = P_2 = 50$–300 MPa were prepared by sintering twice at 825 °C for 6 h under $P_{O2} = 3$ kPa. It has been confirmed that sintered bulks with almost Bi2223 single phase can be prepared under this sintering condition. Fig. 1 shows uniaxial pressure ($P_1 = P_2$) dependence of relative density of the bulks and $T_{c\,(end)}$ determined by a criterion of $\rho = 1\,\mu\Omega$ cm, which is more than three orders of magnitude lower than the normal state resistivity at just above $T_{c\,(onset)} \sim 115$ K. The sintered bulks pressed under high pressure of $P_1 = P_2 > 200$ MPa had higher density, while these samples showed broader superconducting transition and hence lower $T_{c\,(end)}$. It suggested that the grain coupling of the bulks was weaker due to remained cracks caused by pressing. In contrast, the sintered bulk pressed under $P_1 = P_2 = 100$ MPa showed slightly high density (~65%) and higher $T_{c\,(end)}$, which corresponded to the strong grain coupling. $J_{c\,(intergrain)}$ of the bulks pressed under 100 MPa and 300 MPa were estimated to be 3.2 kA cm^{-2} and 0.76 kA cm^{-2}, respectively, at 20 K.

In this fabrication process, the uniaxial pressing under a moderate pressure (~100 MPa) was found to be effective to strengthen the grain coupling by elimination of remaining cracks after second-sintering. Therefore, pressure of the uniaxial pressing was fixed $P_1 = P_2 = 100$ MPa in the subsequent experiments.

3.2. Improving J_c properties by sintering at a low temperature and post-annealing

For further improvement in J_c properties, dependences of sintering and post-annealing conditions on superconducting properties were examined. Heat treatment conditions of the sintered bulk