Microstructure and superconducting properties in air-properties GdBa$_2$Cu$_3$O$_{7-\delta}$ superconductor with the additives of nano particles

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Abstract: It is regarded as an effective method to improve the flux pinning performance by the additives of the secondary phase inclusions in nano sizes into high temperature superconductor bulks. We prepared the single domain superconductor GdBa$_2$Cu$_3$O$_{7-\delta}$ bulks with variable additions of (ZrO$_2$+SnO$_2$+ZnO) nano-particles in air by using top seed melt-textured growth process. The effect of nano-particle additions on superconductivity properties has been investigated. An enhancement of the critical current $J_C$ in low and intermediate field at 77K and trapped field was discovered by the additions of the nano-particles. At the same time, the superconductor transition temperature, $T_C$, slightly decreases from 93.5K to 91.5K. The microstructure measurements show that the nano-particle inclusions enhance with the increase of the content of nano-particles, which may illuminate the $J_C$ enhancement of the specimens.
1. Introduction

Large single-domain RE-Ba-Cu-O superconductors are promising materials for cryogenic applications due to their superior superconducting performance [1, 2, 3]. For the commercialization, it is important to keep the low cost to fabricate while being the high superconducting properties. So as to say, it exhibits the higher critical current density ($J_C$) in the fundamental characteristic of the bulk. Thus, in recent years, various doping of secondary phase particles, such as RE$_2$BaCuO$_5$ (RE211), RE$_2$Ba$_4$CuMO$_y$ (RE2411) and nano-particles etc., are popular to be used. The corresponded nano-sized inclusions and defects in the superconducting matrix are effective as pinning centers to improve $J_C$ of melt-growth bulk superconductors REBa$_2$Cu$_3$O$_7$-$\delta$ (RE123) [4-9]. It is reported that the additions of nano-sized SnO$_2$ or ZrO$_2$ to RE123 matrix, as second phase with Gd211 inclusions, form a three-dimensional band structure to enhance $J_C$ [8]. Lau et al. observed that the Ag-sheathed Bi(Pb)-Sr-Ca-Cu-O tapes with magnetic nano-powder $\gamma$-Fe$_2$O$_3$ increase the pining strength [11]. However, until now, it is unclear for the micro mechanism on the addition effects of nano-sized particles into the bulk RE123 superconductors.

In our work, the single-domain Gd123 bulks with the additions of (ZrO$_2$+SnO$_2$+ZnO) nano-particles was prepared. We expect the improvement of superconducting properties of Gd123 bulks. The study proves that the addition of the nano-sized particles is effective to improve the $J_C$ of the bulk superconductors.

2. Experimental

Commercial powders of Gd$_2$O$_3$ (3N), BaO$_2$ (3N) and CuO (3N) were employed to synthesize single-phased Gd$_2$BaCuO$_5$ (Gd211) by the solid state reaction method. The mixed powder was pre-reacted at 900°C for 10h in air twice. X-ray diffraction was employed to confirm the single phase of the Gd211 powder. In order to reduce the particle size of Gd211, ball-milling treatment has been conducted for 1h, using the Y$_2$O$_3$-ZrO$_2$ balls. Subsequently, the high purity BaO$_2$ powder was added into the Gd123 matrix to suppress the formation of the solid solution due to the substitution between Ba and Gd atoms [12]. To improve the mechanical properties and reduce the coarsening of the Gd211 particles, 10%Ag$_2$O and 0.5%Pt in weight were also added. The nominal composition of the bulk is Gd123 + (0.4-x)Gd211 + x(ZrO$_2$+SnO$_2$+ZnO) + 0.1BaO$_2$ with $x$ = 0.0, 0.006 (labeled as $x$ nano particles), in a molar ratio to Gd123. The mixed powders were pressed into pellets of 20mm in diameter and 10mm in thickness. We use a small air-processed Nd123 crystal with a 1057°C melt-point as the seed of every bulk [13]. The melting process of the bulk superconductors and the post-annealing in argon and oxygen gases has been published in previous reports [8, 12, 14].

The DC magnetization was measured with a Quantum Design SQUID magnetometer. To clarify the influence of the spatial distribution on the superconducting properties, a rectangular slab of 2mm×2mm×1mm were cut along both $ab$ plane and $c$-axis growth direction from each bulk, that is to say, one is under the seed position and another is near the
boundary of the single domain. Moreover, to eliminate the surface defects the slab positioned at 1.5mm below the surface was cut for magnetic characterization. The DC magnetization measurement was investigated under a magnetic field parallel to the \( c \) axis. The critical current density \( J_C \) values were estimated based on the extended Bean’s critical state model for a rectangular sample [15]. Trapped field mapping were performed at 77K with 0.1mm gap between the Hall sensor and the surface of sample and the initially applied magnetization field was selected as 1T. The microstructure was observed by scanning electron microscopy (SEM).

3. Results and discussion

![Figure 1. Surface appearance of the superconductor bulk with 0.006 nano particles (ZrO\(_2\)+SnO\(_2\)+ZnO), melt-processed in air. The sample diameter is 18 mm and the thickness is 7 mm.](image)

3.1 Growth of single domain and the trapped field of the bulks with and without nano-particle additions

Figure 1 shows the photograph taken from the top surface of the superconductor bulk with 0.006 nano particles. They can grow into a single domain with the diameter of 18 mm and the thickness of 7 mm. It will be possible that future optimization of processing condition will enable to fabricate the single-domain with even higher contents of nano particles (ZrO\(_2\)+SnO\(_2\)+ZnO).

Figure 2 shows the trapped fields of the bulk with 0.006 nano-particles (ZrO\(_2\)+SnO\(_2\)+ZnO). The applied field for the bulk was 1 T with field cooling. The trapped field density arrives to 0.10 T in the bulk of 0.006 nano-particle additions, which is higher that 0.06 T in the undoped bulk [14]. It demonstrates that the nano-particle additions enhance
the trapped field of bulks. Therefore, it may result in the enhancement of $J_C$.

**Figure 2.** Trapped field profiles on the field cooling of bulks with 0.006 nano particles (ZrO$_2$+SnO$_2$+ZnO) at 77 K. The initial magnetic field is 1 T. Measurements is done with 0.1 mm gap between the Hall sensor and the surface of samples. The sizes of bulk are 18 mm in diameter and 7 mm in thickness. The highest trapped field density is 0.10 T.

**Figure 3.** Applied magnetic field dependence of $J_c$ of the single domain bulks with 0.0 nano particles (squares) and 0.006 nano particles (ZrO$_2$+SnO$_2$+ZnO) (stars), respectively. $T_C$ positioned near the edge is shown as the open symbols, whereas $T_C$ positioned under the seed is shown as the solid symbols.
3.2 Enhanced superconducting properties of bulks with nano-particle additions

Fig. 3 shows the applied field B dependence on the $J_C$ for the specimens cut at the position near the edge of the bulks at 77 K with the magnetic field B parallel to c axis. The peak effects are not obvious in the $J_C$-B curves, which is probably due to the accumulation of Gd211 particle at the edge of the single domain [16]. There is a significant enhancement in the low magnetic field for the bulk with 0.006 nano particle additions. However, in the high magnetic field, the $J_C$ decreases with the addition amounts of $(\text{ZrO}_2+\text{SnO}_2+\text{ZnO})$ nano particles. The highest $J_C$ value reaches $7,2500 \, \text{A cm}^{-2}$ at the sample with 0.006 nano particles. The kind of nano particle as second phase will be effective flux pinning site in the Gd123 matrix, which is essential to enhance the $J_C$, so as to the superconductor performance [8]. This suggestion also has been illuminated by the image of SEM in Fig. 4. At the same time, it is found that the Zn ion doping for Cu site in the Gd123 system degrade the superconductivity transition temperature and increase the $J_C$ [17, 18]. It illuminates that the Zn ion existence increases the $J_C$ of our specimens.

Fig. 3 also shows the $J_C$ versus applied B for the superconductor bulks positioned under the seed site. It is clear the $J_C$ positioned under the seed site is lower than that positioned near the edge for the same compositions. $J_C$ value is observed to decrease with the additions of $(\text{ZrO}_2+\text{SnO}_2+\text{ZnO})$ nano particles in the high magnetic field. While it remarkably increases in the low magnetic field for the bulk with 0.006 nano particles. The present results may elucidate the spatial variation of the superconductivity properties with inhomogeneous Gd211/nano-particle distributions from seed site to edge position.

![Figure 4. SEM image positioned near the edge for the bulk with 0.0 nano particles (a), the bulk with the additions of 0.006 nano particles $(\text{ZrO}_2+\text{SnO}_2+\text{ZnO})$ (b), respectively.](image)

In order to understand the pinning performance and the distribution of second phase inclusions, we examined the microstructure of the samples positioned near the edge using SEM, as shown in Fig. 4 (a) for the bulk with 0.0 nano particles and (b) for the bulk with 0.006 nano particles. There was a noticeable increase of nano-sized second phase inclusions in white particles for the bulks with 0.006 nano particles in Fig. 4 (b), compared with the bulk with 0.0 nano particles in Fig. 4 (a) [14]. The accumulation of second phase inclusions may form the effective pinning center to illuminate the enhancement of superconductor properties in the bulk with 0.006 nano particles, such as the performance of $J_C$ and trapped field in Fig. 2.
There is no band structure appearance with the additions of nano particles which results in the increase of the superconductor performance, as reported by Xu et al. [8]. The future investigation of the microstructure for the bulk with the nano particles additions are in the study.

Figure 5. Superconducting transition curves, $T_C$, of the single domain bulks with 0.0 nano particles (squares) and 0.006 nano particles (ZrO$_2$+SnO$_2$+ZnO) (stars), respectively. $T_C$ positioned near the edge is shown as the open symbols, whereas $T_C$ positioned under the seed is shown as the solid symbols.

Figure 5 shows the superconducting transition temperature, $T_C$, with different composites containing various amounts of nano particles. It is seen that the onset $T_C$ has a slight decrease from around 93.5 K for the bulks with 0.0 nano particles to around 91.5 K for the bulks with 0.006 nano particles. A low Zn element doping for Cu sites in the Gd-123 system [17, 18] were found to gradually result in the lower $T_C$ of the bulk and enhance $J_C$ in the low magnetic field (Fig. 3). However, the present results illuminate that nano particles additions do not degrade superconductivity of the samples.

4. Conclusion

We fabricated successfully the single-domain superconductor bulks with the nano-particle (ZrO$_2$+SnO$_2$+ZnO) additions, in molar ratio to Gd123, as second phase into Gd123 matrix together with fined Gd211 particles. The superconducting property doesn’t be degraded under the additions with the transition temperature shifting from 93.5 K in the undoped bulk to 91.5 K in the bulk with 0.006 nano particles (ZrO$_2$+SnO$_2$+ZnO). Compared with the undopes bulk, the trapped field and $J_C$ is observed to increase significantly in the bulk with 0.006 nano-particle (ZrO$_2$+SnO$_2$+ZnO) additions. The $J_C$ for 0.006 nano-paticle composites reaches 7, 2500 A cm$^{-2}$, at 77 K and under the self-field. The $J_C$ values may elucidate a spatial variation for the different compositions containing various amounts of nano-particle inclusions from the seeding position to the edge of the single domain. The study
on the microstructure and distribution survey by SEM suggested the richer nano-sized inclusions exist in the bulk with nano-particle 0.06 (ZrO$_2$+SnO$_2$+ZnO) so as to result in the increase of $J_c$.

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