Enhancement of flux pinning in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ bulks prepared by nanoparticle-powder-assisted method

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Abstract: High quality $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$ (Gd123) textured bulks with $\text{Nd}_2\text{BaCuO}_5$ (Nd211) nanoparticle precipitations have been fabricated by a nanoparticle-powders-assisted MTG (melt-textured-growth) technique. The high density nanoscale flux pinning sites were introduced into Gd123 by mixing Nd211 nanoparticle powders (about 20–50 nm) with Gd123 nano-precursors before the MTG process. Microstructural analyses reveal that a large number of Nd211 nanoparticles with a size around 50–150 nm were inserted in the Gd123 matrix, forming a kind of superconducting nanocomposites. The critical current density at 77 K is systematically increased and the flux pinning behavior is significantly improved. The scaling behavior of the flux pinning force shows a magnetic field dependent feature with a peak located at $h_p \approx 0.4$. This may be the fingerprint of melt-textured 123 compounds, which cannot be interpreted by the simple superposition of different types of elementary pinning sources.

Key words: flux pinning; $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$; nanoparticle-powder assisted processing; critical current density

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1. Introduction

Levitation force between a high temperature superconducting bulk and a permanent magnet has many potential applications including flywheels-based energy storage system [1], superconducting bearings [2], transportation [3], and Maglev trains [4].

In the bulk superconductors, the structural defects with dimensions at nanoscale play an important role for flux pinning which supports a high performance in the levitation system [1–4]. For example, in low-temperature superconductors (LTSS) like Nb-Ti and Nb_3Sn , the strongest pinning is supplied by a dense lamellar structure of normal α -Ti ribbons, about 1 nm (0.2ξ , where ξ denotes coherence length) thick and aligned parallel to the wire transport current in Nb-Ti [5], and by grain boundaries in Nb_3Sn [6–8]. In the newly discovered superconductor, MgB_2 , the strong pinning may be also related to the nanoscale grain boundaries and nanoprecipitates [9–13]. In high temperature superconductors (HTSS), due to a short coherence length and an ex-

tremely sensitive dependence of T_c on the hole-concentration in HTSS, a weak hole-depletion at crystalline defects can locally suppress superconductivity, as observed near single-atom impurities (Ni and Zn) in doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$ (Bi2212) single crystals [14], and on scale of 1–2 nm in pure crystals [15–16]. This suggests that nanosize-defects in HTSS may also act as effective core pinning centers. However, the performance of HTSS degrades rapidly with the increasing field and temperature. Up to now, it is still no sure what kinds of pinning centers are suitable to pin the vortices in HTSS to guarantee a high performance at high temperatures (about 77 K) and high fields (≥ 5 T).

It is well-known that HTSS have a layered structure, in which superconducting layers (severed by CuO_2 planes) separated by non-superconducting layers are weakly Josephson coupled to each other. A vortex perpendicular to these layers, which would conventionally be considered a uniform cylinder of confined flux surrounded by circulating currents, is looked upon in HTSS as a stacking of two-dimensional pancake-shaped vortices [17]. At a sufficiently low temperature, the coupling between the pancake vortices is rather strong, making the vortices behave like a “flux line” that can be pinned by a limited number of pinning centers. As the

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Josephson coupling energy decreases with increasing temperature as $E_J \propto (1-T/T_c)^2$, the “flux line” becomes very soft at higher temperatures and cannot be pinned by a few pinning centers. In addition, the typical value of coherence length for HTSs is about 1 nm, which allows point defects, such as isolated vacancies, substitutions, interstitials, etc., to be efficient pinning centers since their sizes match well with the coherence length at low temperatures. With temperature increasing, the coherence length increases, $\xi = \xi(1-T/T_c)^{-1/2}$. At 77 K, it increases to about 3 nm for $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (Y123). In this case, most of the point defects in Y123 can no longer operate as efficient pinning centers at 77 K due to the mismatch between the pinning size and the coherence length. This suggests that structure imperfections with nanoscale around 10 nm may be effective pinning centers at 77 K for Y123 superconductor, which has been demonstrated by adding nanoparticles in Y123 matrix with a size between 20–300 nm [18]. The J_c was significantly improved by the nanoparticle addition; however, the improvement was mainly in the low field region, probably due to that the size of the particles were still too large (the average size is larger than 100 nm). It is interesting to know if the J_c - H behaviour of the high- T_c superconductors can be further improved when the size of nanoparticles is further decreased.

In this paper, high quality $\text{Gd}_2\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ (Gd123) textured bulks with various densities of flux pinning centers have been fabricated by a nanoparticle-powders-assisted MTG (melt-textured-growth) technique. The reason to use Gd123 rather than YBCO is that Gd123 has higher T_c , and its J_c value at 77 K is also greater than that of Y123. In order to achieve a better performance in levitation system, Gd123 is selected in this study. It is found that the J_c - H behaviour in high field region at 77 K is systematically improved with the number density of the nanoscaled precipitates increasing, by adding $\text{Nd}_2\text{BaCuO}_5$ (Nd211) nanoparticle powders (about 20–50 nm) into the nano-precursors of Gd123. The results show that the nanoscaled defects with 50–150 nm may take responsibility for the effective pinning centers in this Gd123+Nd211 superconducting nano-composite system at 77 K.

2. Experimental

The Gd123 and Nd211 nanoparticles were prepared by citrate pyrolysis technique [19], and heated at 780 °C for 10 h. The particle size for most of the Gd123 and Nd211 grains is around 20-50 nm as revealed by transmission electron microscope (TEM). The mixture of precursor nano-powders ($\text{Gd123}+x\text{wt}\%\text{Nd211}$, $x=0, 10, 20$, and 30) were pressed into disks of a diameter 30 mm and thickness of 15 mm, and then pressed again

under hydrostatic pressure of 2 000 kg/cm². The disks were then processed in an isothermal box furnace for a melt-textured growth processing with Nd123 single crystal as a seed on the top of the disk (a typical top-seeded melt-textured) [20]. The as-grown samples were annealed in flowing oxygen atmosphere at 320 °C for 200 h. It is noticeable here that Nd211 rather than Gd211 nanoparticles were used as the addition in this study. Two considerations were involved: the first one is to suppress the growing up of 211-phase nanoparticle in the 123-phase matrix; the second is to build up a sharp phase between the 211- and 123-phases. Since Nd211 has a higher growing temperature than Gd211, the Nd211 particles may grow more slowly than Gd211 particles in the Gd123 matrix.

Crystalline structure was studied by powder x-ray diffraction (XRD) using an X'Pert MRD diffractometer with CuK α radiation. Microstructure was analyzed with a scanning electron microscope (SEM) and a Philips field emission transmission electron microscope with energy-dispersive X-ray spectroscopy (EDX) analysis. Magnetization was measured using a 9 T physical property measurement system (Quantum Design). All the samples used for magnetization measurement was shaped into a size of 0.4 mm $\times$ 0.6 mm $\times$ 1.1 mm cut from the bulk disks. A magnetic J_c was derived from the width of the magnetization loop ΔM (with $H//c$) based on the extended Bean model: $J_c = 20\Delta M/[a(1-a/3b)]$ with $a=0.4$ mm and $b=0.6$ mm.

3. Results and discussion

Fig. 1 shows the typical XRD patterns for the Gd123 powder and textured bulk.

Fig. 1 X-ray diffraction patterns for Gd123 nanopowders and Gd123+10 Nd211wt% melt-textured bulks

The Gd123 powder is quite pure according to the resolution of the XRD. The textured Gd123 bulk shows high grain alignment along the c -axis of the Gd123

crystal. No Nd211 reflection was detected in the XRD analysis probably due to a big difference of the intensity between Gd123 crystal and Nd211. This may also reflect that the Nd211 particles are relatively tiny in the Gd123 matrix, as being confirmed later by the TEM analysis.

Fig. 2 shows the typical results of the temperature dependence of magnetization for Gd123+x wt%Nd211 textured bulks with $x=0, 10, 20$, and 30 . The superconducting transition temperatures for all of these samples studied in this work are almost the same, i.e., $T_c=93.2$ K. This indicates that adding Nd211 does not significantly modify the superconductivity of Gd123 matrix, and is consistent with the EDX analysis for the Gd123 matrix where no trace of Nd was detected. This also reveals that Nd211 phase is thermally stable at the texturing process temperature at 1100°C , and not very reactive with Gd123 at high temperature. However, it is important to note that the transition width, ΔT_c , of the Gd123 matrix in the Gd123+x wt%Nd211 textured bulks has been modified by adding Nd211 nanoparticles. The relation between the Nd211 concentration x and the T_c is depicted in Fig. 3, which illustrates that the ΔT_c changes slowly with increasing the amount of Nd211 up to $x=20$, but suddenly increases a lot at $x=30$, indicating that the addition of Nd211 may modify the composition of Gd123 matrix to a certain extent. This also shows that superconducting transition width is a more sensitive parameter in monitoring the tiny changes of the phase purity, compared to the structural analysis.

J_c - H curves at 77 K for Gd123+x wt%Nd211 textured bulks prepared by the nanoparticle-powder-assisted method are shown in Fig. 4.

Fig. 2 Temperature dependence of magnetization for Gd123+x Nd211wt% melt-textured bulks with $x=0, 10, 20$, and 30 at $\mu_0H=2$ mT. The measurement was done in the zero field cooling (ZFC) with the field parallel to the c direction.

Fig. 3 Variations of irreversibility field, H_{irr} , and superconducting transition width ΔT_c with the amount of Nd211 nanoparticles.

Fig. 4 J_c - H curves at 77 K for melt-textured Gd123+xNd211wt% melt-textured bulks with $x=0, 10, 20$, and 30 at 77 K with the field parallel to the c direction. The inset shows the field dependence of the volume pinning force density for these samples.

In the measurements the applied magnetic field is parallel to the c axis. It is evident that for all of the samples prepared by the nanoparticle-powder-assisted method, the J_c - H behavior at 77 K has been significantly improved with adding Nd211 nanoparticles. In addition, the J_c - H behavior is also improved systematically with increasing Nd211 weight percentage, as reflected by the shifting of the fishtail peak in the J_c - H curves towards higher magnetic fields. At the same time, the degradation of J_c with increasing magnetic field becomes slow. For the samples of 20 wt% Nd211, the J_c peak is located near the field of 3 T, much higher than the sample without Nd211 addition. Besides the enhancement of J_c , the flux pinning force density is also systematically improved (see the inset of Fig. 4), and at the meantime, the irreversibility field, H_{irr} , at 77 K is consequently enhanced (see Fig. 3), indicating that Nd211 addition is an

important way of creating flux pinning centers in Gd123 matrix. However, as shown in Figs. 3 and 4, the changes of the values of J_c and H_{irr} are not monotonic with increasing Nd211 amount. Instead, they are gradually getting saturated as approaching $x=20$ wt%, and begin to decrease at $x>20$ wt%.

In order to understand the pinning mechanism of these samples, the scaling-law analysis proposed by Dew-Hughes [7] was used to analyze the flux pinning force, which gives

$$F_p(h) = F_p / F_{p,max} \propto h^p (1-h)^q, \quad (1)$$

where $F_{p,max}$ is the maximum volume pinning force, h the reduced field H/H_{irr} , and the parameters p and q the characteristic exponents reflecting flux pinning types. There are six different pinning cases describing the elementary pinning force using Eq. (1) with: (1) $p=0$, $q=2$: normal core pinning, volume pins, the peak position is at $h_p=0$; (2) $p=1$, $q=1$: Δk -pinning, volume pins, the peak position is at $h_p=0.5$; (3) $p=1/2$, $q=2$: normal core pinning, surface pins, the peak position is at $h_p=0.2$; (4) $p=3/2$, $q=1$: Δk -pinning, surface pins, the peak position is at $h_p=0.6$; (5) $p=1$, $q=2$: normal core pinning, point pins, the peak position is at $h_p=0.33$; and (6) $p=2$, $q=1$: Δk -pinning, point pins, the peak position is at $h_p=0.67$.

It is generally believed that the so-called point core pinning (i.e., the flux pinning related to non-superconducting point defects embedded in the superconducting matrix) is of a value of $h_{max} \approx 0.33$, but the so-called volume Δk -pinning (i.e., the flux pinning related to the spatial variation of the Ginzburg-Landau parameter κ in the superconductivity matrix) has a value of $h_{max} \approx 0.5$ [21]. As shown in Fig. 5, the scaling behavior, $F_p(h)-h$, for all the Gd123+Nd211 samples of different Nd211 amount is the same, with the peak value $h_p \approx 0.4$. This is very close to the value of $h_p=0.42$ for melt-textured NdBa₂Cu₃O₇ (Nd123) [21] and melt-textured Y123 with fine Y211 particles [22], but quite different from the value of $h_p=0.5$ for Nd123 single crystals [21]. The results may hint that $h_p \approx 0.4$ is a fingerprint of the pinning behavior for the high- T_c superconducting melt-textured bulks.

In order to understand the pinning mechanism of Gd123+Nd123 system, its $F_p(h)-h$ scaling feature is analyzed according to Eq. (1). The best fit for the $F_p(h)-h$ behavior of Nd123 melt-textured bulks is $p=1.48$ and $q=2.23$ [21]. For our system, using the similar parameters $p=1.5$ and $q=2.25$, the experimental data can be roughly fitted (see Fig. 5). A better fit yields $p=2.21$ and $q=3.35$, as also shown in Fig. 5.

No matter $p=1.48$ and $q=2.23$ or $p=2.21$ and $q=3.35$, the scaling behavior is quite different from what Dew-

Fig. 5 F_p-h scaling behavior at 77 K with field parallel to the c direction for Gd123+ x Nd211wt% melt-textured bulks with $x=0, 10, 20$, and 30 . Two fitting curves of the experimental data with Eq. (1) are also presented.

Hughes proposed elementary pinning force types (see Fig. 6). This means that the pinning mechanism inside the system is very complicated. It is quite possible that several elementary pinning mechanisms cooperate in the system simultaneously. Several modified models including the superposition of several pinning mechanisms [23], the shift of H_{irr} [24], and the combination of both [25] were proposed to fit and interpret the experimental data of the scaling behavior for high- T_c Bi2223 superconductors and also MgB₂ superconductors. However, these models are hardly to fit the data for the 123-type high- T_c superconducting melt-textured bulks because the pinning sources are much more complicated in this system. As in other high- T_c superconductors, core pinning is also dominant in the 123-type high- T_c superconducting melt-textured bulks due to their large k values. Therefore, the possible pinning types should be either the nonsuperconducting particles embedded in the superconducting matrix, which trap the flux lines in these nonsuperconducting areas, or $\delta T_c(\Delta k)$ pinning which originates from the spatial variations of the Ginzburg parameter associated with fluctuations in the transition temperature T_c [26]. It can be seen from the comparison of the F_p-h scaling behavior for the melt-textured Gd123+ x Nd211wt% melt-textured bulks with the Dew-Hughes proposed elementary pinning force types, that the Δk -pinning with volume pins ($p=1$, $q=1$) is dominant at low field region but normal point pins get dominant at high field region. It means that the pinning feature is field dependent and cannot be described with a simple superposition of different types of elementary pinning sources. New theories or models are necessary to better describe the pinning behavior for these 123-type high- T_c superconducting melt-textured bulks, which will be reported in our forthcoming researches.

Fig. 6 Comparison of the F_p - h scaling behavior for the melt-textured $\text{Gd123}+x$ Nd211 wt% melt-textured bulks with the Dew-Hughes proposed elementary pinning force types

Fig. 7 TEM micrograph showing Nd211 particle of a size about 150 nm in the Gd123 matrix in the sample of $x=20$

The microstructural analysis revealed that these samples contain many Nd211 particles with dimensions from 50 to 150 nm, as typically shown in Fig. 7.

The phase boundary between Gd123 and Nd211 is very sharp, which is benefit to the enhancement of flux pinning efficiency. However, the Nd211 particles in the Gd123 matrix are significantly larger in size than the Nd211 nano-precursors (20–50 nm) used as raw materials for making the melt-textured bulks, indicating a possible interaction between Gd123 and Nd211 at high temperatures. Fortunately, the Nd211 particle size in the present system is still smaller than that in the samples prepared with conventional melt texture process [18], demonstrating that nanoparticle-powder-assisted method is an effective way to achieve nano-pinning centers in melt-textured 123-type superconducting bulks. It is also

observed that the average particle size of Nd211 increases with the amount of Nd211 addition. Some Gd211 particles with a size larger than 1 μm are observed in the sample with $x=30$. The origin of these Gd211 is not clear but may be induced by Nd211 as a nucleation center. This causes the composition deviation of Gd123 matrix from its stoichiometry, and consequently increases its superconducting transition width, as shown in Fig. 3. Further studies are necessary to clarify its growing mechanism.

4. Summary

High quality Gd123 textured bulks with Nd211 nano-scale pinning sites of 50–150 nm have been fabricated by the nanoparticle-powders-assisted MTG (melt-textured-growth) technique. The nano-pinning-sites structure were achieved by mixing Nd211 nanoparticle powders (about 20–50 nm) with the Gd123 nano-precursors before MTG process. TEM analyses confirm the existence of the Nd211 nanoparticles embedded in the Gd123 matrix with the particle size increasing with the amount of Nd211 additives. As a result, the critical current density at 77 K is systematically increased and the pinning behavior is significantly improved. The scaling behavior of the flux pinning force shows a magnetic field dependent feature with a peak located at $h_p \approx 0.4$. This may be the fingerprint of melt-textured 123 compounds, which cannot be interpreted by the simple superposition of different types of elementary pinning sources.

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