Development of technology for a reliable fabrication of LRE-123 materials for levitation applications above 80 K

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Received 23 November 2004; accepted 19 January 2005
Available online 11 July 2005

Abstract

Nanoscale secondary phase Gd$_2$BaCuO$_5$ “Gd-211” particles less than 60 nm in size, added to mixed ternary LRE-Ba$_2$Cu$_3$O$_{y}$ [LRE = (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$), (Sm$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$), (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)] “NEG-123, SEG-123, NSG-123” oxide powders and melt-processed in Ar–1%pO$_2$ gas mixture, significantly improve electromagnetic performance at low magnetic fields. As confirmed by transmission electron microscopy and dynamic force microscopy, the nanoparticles in the LRE-123 matrix not only survive the melt-texturing process but, thanks to their contamination by Zr coming from ball milling process, these particles in majority transform into a new type of even smaller defects. Further improvement in flux pinning was reached when both 123 and 211 powders were thoroughly ball milled before the melt-growth process to the similar small size. As a result, $J_c$ values of 260 kA/cm$^2$ and 55 kA/cm$^2$ were observed in remnant state at 77 K and 90 K, respectively.

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PACS: 74.80.Bj; 74.60.Jg; 74.60.Ge

Keywords: Microstructure; Critical current density ($J_c$); Flux pinning; Levitation at 90.2 K; LRE-123 melt textured compounds

1. Introduction

LRE–Ba$_2$Cu$_3$O$_y$ “LRE-123” high-$T_c$ bulk superconductors prepared by melt-texturing process approach the stage of industrial applicability.
Most of the hitherto proposed applications have relied on liquid nitrogen cooling. The recent progress in technology of ternary LRE-123 compounds proved feasibility of levitation experiments at liquid oxygen temperature (90.2 K) [1]. Thus, a rather broad range of temperatures above 77 K opened where the new materials can be safely used in the form of permanent magnets [2,3]. The high-$T_c$ magnets will form a basis of an economically reasonable technologies of magnetic separation for removal of environmentally hazardous or inconvenient material components, water quality recovery, sewage-containing water treatment, oil and seawater recycling, etc. [4]. A similar procedure can be applied for used-water cleaning in closed-cycle technological systems, big buildings, etc. [5]. The most challenging task is the potential future use of bulk superconducting magnet technology in magnetically levitated vehicles (MAGLEV’s). The switch from liquid helium to liquid nitrogen cooling will dramatically reduce the cost of operation [6]. Powerful bulk magnets can assist in creating necessary magnetic fields in various medical diagnostic equipments, magnetic excitation units, superconducting energy storage, or ship propulsion [7,8].

The size reduction of non-superconducting pinning centers significantly below 0.1 μm range, recently achieved in NEG-123 compounds with Nd:Eu:Gd = 1:1:1 proved that mesoscopic (nanometer-scale) precipitates were able to cause an exceptional $J_c$ enhancement up to very high temperatures [1]. The outstanding pinning performance of the Zr-based new nanoparticles enabled levitation of a permanent magnet both over and below the NEG-123 superconductor cooled by liquid oxygen (90.2 K). Although levitation experiments at 90.2 K have already been realized, the safety margins needed for practical applications require a further improvement in flux pinning in these materials. Also the technology reliability needs to be tested.

Here we report on the flux pinning enhancement in NEG-123 composite formed by a mixture of ball milled both the superconducting (NEG-123, SEG-123, and NSG-123) and the normal Gd-211 phases.

2. Experimental

High-purity commercial powders of Nd$_2$O$_3$, Sm$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$ and CuO were mixed in the nominal compositions of (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)-123, (Sm$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)-123, and (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)-123. The starting powders were thoroughly ground and calcined at 870 $^\circ$C for 20 h, then pressed into pellets. Sintering was performed at 890 $^\circ$C for 15 h. This process was repeated three times under controlled oxygen partial pressure (pO$_2$) of Ar/1%pO$_2$. In the second step, the powders of Gd$_2$O$_3$, BaO$_2$, and CuO were mixed in the nominal composition of Gd$_2$BaCuO$_5$ and calcined three times at 840 $^\circ$C, 870 $^\circ$C and 900 $^\circ$C for 10 h. The calcined Gd-211 powders were milled using Y$_2$O$_3$–ZrO$_2$ balls in acetone for 0.3–6 h. The average size of the ball-milled powders was 200–60 nm after 0.3–6 h milling, as confirmed by Brunauer–Emmerit–Teller (BET) specific area measurements [9]. 40 mol% of the ball-milled Gd-211 were added to the sintered SEG-123 and NSG-123 powders. In order to suppress coarsening of the Gd-211 particles during the melt process, 0.5 mol% Pt and 1 mol% CeO$_2$ were added. In the case of the NEG-123 combination, the NEG-123 powder was also ball-milled (200 nm size) before the melt-growth process and mixed with 30 mol% Gd-211 (60 nm).

The powder mixtures were pressed into pellets of 20 mm diameter and subject to a cold isostatic pressing under 200 MPa. Finally, a MgO $<100>$ seed was placed at the top center of each pellet, which was then melt-grown in the oxygen controlled atmosphere (OCMG process) of Ar/1%pO$_2$ at a gas flow rate of 200 ml/min. Details of the heat treatment were presented in Refs. [1,10]. For magnetic measurements small specimens with dimensions of $a \times b \times c = 1.5 \times 1.5 \times 0.5$ mm$^3$ were cut from the pellets and annealed in flowing oxygen in the temperature range 300–600 $^\circ$C.

Microstructure of these samples was studied by scanning electron microscope (SEM) and dynamic force microscope (DFM). An atomic-resolution high-angle annular dark field (HAADDF) scanning transmission electron microscopy (STEM) was used to check the dispersion of nanometer-sized
particles. The compositional variation in the nanoparticles was checked by bright field (BF)—STEM images. The energy dispersive X-ray analysis (EDX) associated with STEM-HAADF was employed to estimate the exact chemical composition of the nanoparticles. Magnetization hysteresis loops \((M - H_a)\) loops in fields from \(-2\) to \(+7\) T were measured at \(77\) K to \(90\) K using a commercial SQUID magnetometer (Quantum Design, model MPMS7). \(J_c\) values were estimated based on the extended Bean’s critical state model for a rectangular sample [11].

3. Experimental results

Evolution with increasing temperature of the field dependence of super-current density, \(J_c\) for the latter NEG-123 sample with 30 mol\% Gd-211 is shown in Fig. 1. The \(J_c(\mu_0 H_a)\) curves were deduced from SQUID magnetometer measurements in temperature range of \(70–89\) K in applied field parallel to the \(c\)-axis. In this sample, the initial average sizes of the secondary phase and 123 particles were 60 and 200 nm, respectively. \(J_c\) values of 260 kA/cm\(^2\) and 120 kA/cm\(^2\) at \(0\) and \(3\) T, respectively were achieved at \(77\) K. The super-current density both at low and intermediate magnetic fields significantly improved as compared to earlier reports [1]. Only the irreversibility field slightly decreased. This may be due to the excessive Zr contamination of the Gd-211 and NEG-123 secondary phase. The earlier report [12] clarified that optimum Zr content and particle size are key factors in improving flux pinning performance at high temperatures (>77 K).

The critical current density at \(77\) K of the other composites, SEG-123 and NSG-123 with addition of 40 mol\% Gd-211 secondary phase, are presented in Fig. 2. For comparison, the NEG-123 data from Ref. [1] and those of the sample from Fig. 1 were also added. In all these samples the initial average secondary phase size was around 70 nm and the powder was mixed with the sintered un-milled 123 powders. In all these systems the low-field super-current density at \(77\) K is high. However the high-field pinning performance
varies, probably in dependence of the actual matrix chemical ratio and light rare earth distribution [13].

Fig. 3 shows the dynamic force microscope (DFM) image of the SEG-123 sample (the initial average Gd-211 particle size of around 70 nm) that indicates uniform nanoparticle distribution in the final product. Majority of the particles were less than 100 nm in size, many even less than 50 nm. The effect looked similar to that previously observed in the NEG-123 sample with 40 mol% Gd-211 [14], where most nanoparticles of 20–50 nm in size consisted of a Zr-contaminated new compound. To test this point in the SEG-123 system, we studied the nanoparticle chemical composition using the atomic-resolution high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The results are in Fig. 4. Size of the nanoparticles varied between 20 and 60 nm and the particles were

![Dynamic force microscope image](image1)

Fig. 3. Dynamic force microscope image of the (Sm0.33Eu0.33Gd0.33)-123 sample with 40 mol% Gd-211 (70 nm). Note the uniform dispersion of nanometer-size particles in the SEG-123 matrix. The image shows that the final particle diameter ranges from 40 to 100 nm.

![HAADF-STEM image](image2)

Fig. 4. The HAADF-STEM image of the sample from Fig. 1. In the inset, dark (RE,Zr)BaCuO	extsubscript{y} particles of 20–40 nm size within large Gd-rich SEG-211 particles are clearly visible.
distributed throughout both the superconducting matrix and much larger particles of secondary phases (300–1500 nm in size—see inset of Fig. 4). STEM by EDX analysis confirmed that the large particles are Gd-211 and Gd-rich SEG-211. Most nanoparticles (40–60 nm in size) consisted of a new phase \( \text{LRE–Ba}_2\text{CuZrO}_y \) [LRE = (Sm, Eu, Gd)] and the particles smaller than 30 nm were of \( \text{(LRE, Zr)}\text{BaCuO}_y \). The more detailed information on chemical analysis is reported in Ref. [15]. We can thus conclude that the positive effect of Zr on electromagnetic performance works in all ternary LRE-123 melt-textured compounds. Zr somehow inhibits both the particles coarsening and their complete dissolution in the ambient material. The Zr-based nanoparticles thus represent an effective pinning medium, especially appropriate for low magnetic fields and high temperatures, extending up to boiling point of liquid oxygen. Fig. 5 presents conventional levitation experiments at liquid oxygen temperature with a permanent Fe–Nd–B magnet levitating above the NEG-123 from Ref. [1] (top figure), SEG-123 (middle figure), and NSG-123 (bottom figure). From Fig. 2 it follows that the ball milling of both Gd-211 and the LRE-123 material allows for even better magnetic flux pinning and gives thus the necessary safety margins for bulk superconducting magnets applications at temperatures above 80 K.

Our calculations of the remanent state trapped field, using \( J_c \) data measured on the NEG-123 sample from Ref. [1] and sample dimensions (diameter \( d \) and thickness \( t \), \( d \times t = 5.5 \times 2 \text{ cm}^2 \)), give values exceeding 5 T and 0.5 T at 77 K and 90 K, respectively. This is nearly half magnet size of that previously considered for use in MagLev applications. A further extension of the safety margins can be realized by setting the operation temperature slightly below liquid nitrogen, e.g. 70 K and using efficient cryogen-free refrigerators.

4. Summary

In summary, generation of compact high-performance superconducting magnets for high-temperature operation becomes realistic due to improvement of flux pinning of ternary melt-textured LRE-123 materials. HAADF-STEM and STEM by EDX HAADF analyses proved that
nanometer-sized Zr-rich particles persisting in both the LRE-123 matrix and inside larger LRE-211 precipitates in all NEG-123, NSG-123, and SEG-123 composites are quite the same as those observed originally in the NEG-123 and SEG-123 systems [1,15], being composed of LRE–Ba$_2$CuZrO$_y$ and (RE,Zr)BaCuO$_y$. The enhanced pinning appeared in all the investigated mixed ternary 123 systems and persisted up to liquid oxygen temperature. Combination of ball-milled Gd-211 and LRE-123 powders lead to critical current density by more than 35% higher value than the previous record. This provides a new potential for improving the melt-processed LRE-123 materials for permanent magnet industrial applications in the temperature range 70–90 K.

References