Superconducting levitation at 90 K—a base for construction of non-contact liquid oxygen pumps

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Received 3 September 2004, in final form 3 September 2004
Published 6 December 2004
Online at stacks.iop.org/SUST/18/S47

Abstract

We report on a new type of nanometre-scale pinning defect in melt-processed (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_y$ ‘NEG-123’ with a Gd$_2$BaCuO$_5$ (Gd-211) addition. A reasonable amount of the Gd-211 particles refined by long-term ball milling to about 70–200 nm reduced their size during the melt-texturing process down to 20–50 nm. Chemical analyses revealed that these particles contained a significant amount of zirconium. These particles caused $J_c$ enhancement by an order of magnitude not only at 77 K but also at 90 K. As a result, we could levitate a permanent magnet over the (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_y$ superconductor cooled by liquid oxygen. This is a path to non-contact pumps of liquid oxygen for different fields of practice.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Most bulk superconductor applications such as superconducting motors, magnetic separators, magnetic bearings, transport systems, and other devices have been operated at or below liquid nitrogen temperature. These applications require a good vortex pinning performance and the associated high critical current density. In melt-processed compounds two classes of defects play a principal role, point-like ones (nm-scale), active mainly in intermediate and high fields, and large normal particles (µm-size), effective in low magnetic fields. The pinning efficiency of large particles is inversely proportional to their size. Thus a control over pinning size distribution leads to flux pinning governing in these materials. In melt-processed YBa$_2$Cu$_3$O$_y$ samples a simultaneous pinning by large Y$_2$BaCuO$_5$ ‘Y-211’ inclusions and point-like oxygen-deficient clusters yielded the critical current density, $J_c$, in the range of $10^4$ A cm$^{-2}$ at 77 K and fields of a few teslas [1, 2].

Surprisingly, a similar compound, NdBa$_2$Cu$_3$O$_y$, ‘Nd-123’, has been found to produce systematically better flux pinning in intermediate fields [3]. A microstructure study revealed that Nd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ (Nd123ss) clusters of 20–50 nm size were dispersed in the Nd-123 matrix [4] and the presence of such clusters contributes to a dramatic enhancement of flux pinning at high temperatures and in high fields. It has been found that a similar fluctuation is inherent to all LREBa$_2$Cu$_3$O$_y$ ‘LRE-123’ materials where the light rare earth ‘LRE’ forms an LRE–Ba solid solution. As a result, a strongly developed secondary peak is usually observed in all LRE-123 materials [5].

Here we report on our attempt to enhance the pinning performance of (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_y$ by refinement of Gd-211 particles with a long-term milling.

2. Experimental details

High-purity commercial powders of Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$ and CuO were mixed in a nominal composition of (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$. The starting powders were thoroughly ground and calcined at 880°C for 20 h with...
intermediate grinding, then pressed into pellets. Sintering was performed at 900 °C for 15 h. This process was repeated three times under controlled oxygen partial pressure (pO2) of 1% O2. In the second step, powders of Gd2O3, BaO2, and CuO were mixed to have a nominal composition of Gd2BaCuO5 and calcined twice at 840 and 900 °C for 4 h. The calcined Gd-211 powders were milled using Y2O3–ZrO3 balls in acetone for 0.3–4 h. The average size of the ball-milled powders was 200–70 nm after 0.3–4 h milling, as confirmed by Brunauer-Emmet-Teller (BET) specific area measurements [6]. 30 and 40 mol% of the ball-milled Gd-211 were added to the sintered NEG-123 powders. In order to suppress possible coarsening of the Gd-211 particles during melting, 0.5 mol% Pt and 1 mol% CeO2 were added. The powder mixture was pressed into pellets of 20 mm diameter and subjected to a cold isostatic pressing under 200 MPa. Finally, an MgO (100) seed was placed at the top centre of the pellet, which was then melt-grown in an oxygen controlled atmosphere (OCMG process) of Ar and 1% pO2 at a gas flow rate of 200 ml min⁻¹. Details of the heat treatment were presented in [7]. For magnetic measurements small specimens with dimensions of a × b × c = 1.5 × 1.5 × 0.5 mm³ were cut from the pellets and annealed in flowing oxygen in the temperature range 300–600 °C [7]. The microstructure of these samples was studied with a dynamic force microscope (DFM) and a transmission electron microscope (TEM). The chemical composition of the matrix was analysed by energy dispersive x-ray spectroscopy (EDX). Magnetization hysteresis loops (M–H loops) in fields from −2 to +7 T were measured at 77 K using a commercial SQUID magnetometer (Quantum Design, model MPMS7). Jc values were estimated based on the extended Bean critical state model for a rectangular sample [8].

3. Results and discussion

3.1. Magnetic performance

In figure 1, we present the Jc(H) performance of the NEG-123 samples with an initial amount of 30 mol% of Gd-211 powder with an average particle size ranging from 200 nm (ball-milled for 0.3 h) to 70 nm (ball-milled for 4 h), measured at 77 K for H∥c-axis (top figure). For comparison we have also included the data of a sample with a commercial Gd-211 powder ‘CP’ with an average size of grains <3 μm. One can see a dramatic increase of remnant Jc with increasing ball milling time (decreasing size of the particles). The sample with the average starting particle size of 70 nm exhibited a remnant Jc of 140 kA cm⁻². The supercurrent density further increased with increasing Gd-211 content; in particular, for the particles ball-milled for the longest time, 4 h, the density increased to 30–40 mol%. In this case Jc at 77 K for H∥c-axis reached 192 and 110 kA cm⁻² at remnant state and 3 T, respectively (bottom figure). The insets in both the top and bottom graphs of figure 1 show the Jc(H) performance of the same samples at 90 K for H∥c-axis. The remnant Jc values were dramatically improved to the order of 10³ A cm⁻², indicating a possible use of these materials for levitation at liquid oxygen temperature (90 K). The present results are by more than 60% better than the previous record values for NEG-123 and other RE-123 materials. A similar trend was also observed in the sample with 10 mol% Gd-211 (70 nm) added.

Figure 1. Field dependence of critical current density for (Nd, Eu)Ba2Cu3Oy samples with 30 mol% Gd-211 (top figure) and 40 mol% Gd-211 (bottom figure) refined by ball milling for 0.3 to 4 h (200–70 nm). ‘CP’ represents commercial Gd-211 powders. All the samples were measured at T = 77 K for H∥c-axis. Note that the current density increased with increasing the ball milling time in the whole field range (upper figure). The remarkable current densities of 192 and 110 kA cm⁻² at zero field and 3 T, respectively, were achieved (lower figure, 77 K, H∥c-axis). Both top and bottom insets present the electromagnetic performance at 90 K, H∥c-axis.

One can see that not only the remnant Jc value but also the values at intermediate fields significantly increased with increasing ball-milling time and the amount of the finest particles. This indicates a significant enhancement of pinning by point-like defects. However, even the minimal initial average size of the introduced particles, 70 nm, does not allow considering these defects as point-like ones.

3.2. Microstructure and chemical microanalyses

In order to understand this, we performed microstructure and chemical analyses. Figure 2 shows DFM images of the sample with 30 mol% Gd-211 (70 nm) viewed from the [00l] direction. The secondary phase particles are regularly spread over the NEG-123 matrix (left side). A higher magnification (right side) brought evidence of a significant amount of fine particles with the size ranging between 20 and 50 nm. Such small defects produced spontaneously in RE-123 materials have not been observed. A similar microstructure was also observed in the sample with 40 mol% Gd-211 (figure 3).
Table 1. TEM-EDX results for NEG-123 sample with addition of 30 mol% Gd-211 (average particle size is 70 nm) + 0.5 mol% Pt + 1 mol% CeO$_2$. The diameter of the analysed spot was about 2–3 nm. All analysed particles were less than 50 nm.

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Figure 2. Dynamic force microscope images of the (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_{y}$ samples with 30 mol% Gd-211 (70 nm). Note the nanometre-scale particle dispersion in the NEG-123 matrix.

Figure 3. Dynamic force microscope images of the (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_{y}$ samples with 40 mol% Gd-211 (70 nm). Note the nanometre-scale particle dispersion in the NEG-123 matrix similar to the 30 mol% Gd-211 (70 nm).

Figure 4 shows TEM micrographs of the sample with 30 mol% Gd-211 (70 nm). Two types of nanoparticles can be seen: large irregular inclusions of about 300–500 nm in size and round particles of 20–50 nm size. The scanning TEM-EDX analysis was made on the particles of different sizes and shapes. The analysed spot had diameter of 2–3 nm. More than 65 nanoparticles were analysed. The quantitative analysis by TEM-EDX clarified that the large particles are Gd-211/Gd-rich-NEG-211, which is in good agreement with our earlier studies of the NEG-123 system. In contrast, the defects with size smaller than 50 nm contained a significant amount of Zr. These defects are marked in figure 4 by arrows. A similar feature was observed on several parts of the sample. As no zirconium was intentionally introduced into the sample, we conclude that the Zr contaminated the secondary phase powders during the ball-milling process. To estimate the Zr content in the Gd-211 powders, we made very precise quantitative analysis by inductively coupled plasma spectroscopy (ICP model: SPS-1700HVR). The average content of Zr was found to be 0.23 wt% for 4 h ball-milled Gd-211 powders. The results of the chemical analysis are summarized in table 1.

3.3. Levitation experiments

Figure 5 shows simple levitation experiments performed at liquid oxygen temperature with Y-123 and NEG-123 bulks. In the case of Y-123 the levitation experiment at 90 K was not possible (left figure). The main reason for this failure is that the transition temperature is only slightly above 90 K. In
Figure 4. Transmission electron micrographs of the same material as in figure 2; scale bar: 500 nm. The black arrows in both figures show some nanometre-size Zr based new pinning media found to be RE–Ba–Cu–Zr–Pt–O/RE–Ba–Cu–Zr–O.

Figure 5. A permanent Fe–Nd–B magnet stably levitates over an NEG-123 + 40 mol% Gd-211 (average particle size is 70 nm) superconductor at liquid oxygen temperature (90 K), after the superconductor had been magnetized by the stray field of the permanent magnet and cooled down to 90 K (right figure); the same experiment with a Y-123 superconductor (left figure). Note that we cannot perform levitation at 90 K using the Y-123 superconductor.

Figure 6. NEG-123 ‘permanent’ magnet suspended below another NEG-123 superconductor cooled to 90 K (left figure). For comparison (right figure), an MPMG processed Y-123 pellet is cooled to 77 K and suspended below Fe–Nd–B magnet, using the attractive force between the superconductor and the magnet.

the newly developed NEG-123 with 30 and 40 mol% Gd-211 (with initial size of 70 nm) both $T_c$ well above 90 K and a sufficiently good pinning efficiency at this temperature made the levitation experiment successful (right figure). One can see that the Fe–Nd–B magnet stably levitated above the NEG-123 superconductor at 90 K, similarly to a Y-123 pellet cooled to 77 K [9]. The trapped field providing the potential well for the magnet levitation was strong enough even at 90 K to enable another NEG-123 superconducting magnet to be suspended below the first NEG-123 block (left side of figure 6), similarly to a Y-123 superconductor cooled to 77 K and suspended below a permanent Fe–Nd–B magnet (right side of figure 6).
comparison clearly demonstrates the superiority of ternary LRE-123 compounds to Y-123. The magnetic levitation at liquid oxygen temperature is a direct link to the construction of a non-contact pump for liquid oxygen.

4. Summary

We prepared a new (Nd, Eu, Gd)Ba$_2$Cu$_3$O$_y$ superconductor with 40 mol% of Gd-211 particles refined by ball milling. Due to the fine pinning structure the new material exhibited $J_c$ values of 192 and 110 kA cm$^{-2}$ at remnant state and 3 T (77 K, $H \parallel c$-axis) and a remnant value at 90 K of the order of $10^4$ A m$^{-2}$, which is sufficiently high enough for levitation experiments at liquid oxygen temperature. Microstructure analysis by DFM and TEM revealed a new type of pinning particles 20–50 nm in size uniformly dispersed in the NEG-123 matrix. TEM by EDX analysis identified these small pinning defects to be Zr-rich LRE–Ba–Cu–Pt–O compound. This new structure is a very effective pinning agent in low and intermediate fields (up to 4 T). The obtained results demonstrate the feasibility of new applications at liquid oxygen temperature (90 K).

Acknowledgment

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) as Collaborative Research and Development of Fundamental Technology for Superconductivity Applications.

References