Magnetic levitation in liquid oxygen and its applications

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Abstract
Combination of extremely fine Gd-211 particles and the LRE/Ba solid solution pinning disorder in a melt processed (Nd0.33Eu0.33Gd0.33)Ba2Cu3Oy, followed by an optimal oxygenation resulted in outstanding electromagnetic performance of the material. Transmission electron microscopy with energy dispersive X-ray analysis identified nanometer scale Zr-rich NEG–Ba–Cu–O particles. These were evidently responsible for a substantial increase of the critical current density at 77 K and the rise by an order of magnitude at and above 90 K. Efficient field trapping ability at 90.2 K enabled new NEG-123 magnet to be for the first time employed in levitation at liquid oxygen.

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1. Introduction
Construction of high temperature superconducting permanent magnets sets pretentious demands on production of large single-grain materials with a high pinning performance and mechanical strength [1–4]. To date, the above requirements are best satisfied in LREBa2Cu3Oy “LRE-123” (LRE: light rare earth, Nd, Eu, Gd, Sm) compounds, especially those produced by the oxygen-controlled melt-growth process [5]. Microstructure studies revealed dispersion of nanometer-size clusters in the LRE-123 matrix [6]. According to micro-chemical analysis, they consist of LRE-rich LRE1+xBa2−xCu3Oy “LRE-123ss” superconducting phase. Their role is similar to oxygen deficient clusters in YBa2Cu3Oy “Y-123” single crystals: they are responsible for the formation of secondary peak on magnetization curve [7]. As all light rare earths form a solid solution with barium, the strong pinning due to LRE1+xBa2−xCu3Oy clusters appears also in the mixed LRE-123 (LRE: NEG, NSG) materials [8,9]. In the mixed compounds the possibility to vary the concentration ratio of the LRE elements on the RE site provides an additional degree of
freedom. In a narrow range of the Nd:Eu:Gd ratio values microstructure analysis revealed a new type of pinning centers on nanometer scale. These proved to be very efficient pinning agent at high fields, leading to a significant enhancement of irreversibility field, $B_{irr}$ at 77 K [10].

The melt process technology enables an additional modification of the RE-123 material properties by introducing relatively large (micrometer or sub-micrometer size) non-superconducting secondary phase particles, LRE$_2$ BaCuO$_5$ “LRE-211” [11]. These proved to be effective pins especially at low fields. Their efficiency is inversely proportional to the average particle size. Recently, we succeeded in significantly reducing the LRE-211 particle size by ball milling and thereby improved the flux pinning performance [12].

Here we present results of the Gd-211 particle size reduction via ball milling in the bulk NEG-123 material. This approach caused such a flux pinning enhancement up to 90.2 K that levitation of Fe–Nd–B magnet was possible by the NEG-123 superconductor cooled by liquid oxygen.

2. Experimental

Bulk samples of (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ with 30 mol% Gd$_2$BaCuO$_5$ Gd-211 were prepared using the oxygen-control-melt-growth “OCMG” process in Ar with 1% partial pressure of oxygen. The preparation procedure was described in Ref. [12]. To study the size effect of the initially added Gd-211 particles on flux pinning, Gd-211 powder was ball milled by means of Y$_2$O$_3$–ZrO$_3$ balls in acetone for 0.3–8 h. Subsequently, the milled particles were separated from the balls using a mesh and dried for several hours at room temperature. The average size of the ball-milled particles was 200—<70 nm, depending on the milling time. The size was estimated by Brunauer–Emmerit–Teller (BET) specific area measurements [13]. Before melt processing, 30 mol% of milled Gd-211 particles were thoroughly mixed with the NEG-123 powder. In order to suppress the coarsening of Gd-211 particles during melt processing, 0.5 mol% Pt and 1 mol% CeO$_2$ was added. The crystallization process was initialized by a MgO(1 0 0) seed which was placed at the top center of the pellet. The samples were prepared in a routine manner as described in Ref. [8].

For magnetic measurements small specimens with dimensions of $a \times b \times c \approx 1.5 \times 1.4 \times 0.5$ mm$^3$ were cut from as-grown pellets and annealed in flowing O$_2$ gas in a temperature range of 300–600 °C [8]. Microstructure of these samples was studied with a transmission electron microscope (TEM) and a dynamic force microscope (DFM). Magnetization hysteresis loops (MHL) were measured from 73 to 90 K using a commercial SQUID magnetometer (Quantum Design, model MPMS7) in the field range −2 to +7 T. To minimize the field inhomogeneity, the scan length was restricted to 1 cm. The external magnetic field was applied parallel to the c-axis of the samples. The magnetic $J_c$ values were estimated based on the extended Bean critical state model [14].

3. Result and discussion

Fig. 1 shows the field dependence of the critical current density, $J_c(H_a)$, of the NEG samples with the starting average particle size between 200 and <70 nm. All three samples were measured with a SQUID magnetometer in the temperature range from 73 to 90 K, for $H_a || c$-axis. The sample with starting average particle size 200 nm exhibited the remnant $J_c$ values 83, 68, 52 and 7 kA/cm$^2$ at 73, 77, 80, and 90 K, respectively. The remnant critical current density was improved with decreasing size of the starting Gd-211 powder. For the lowest size of <70 nm, the record remnant critical current density values of 238, 190, 122, and 39 kA/cm$^2$ were achieved at 73, 77, 80, and 90 K, respectively. The above results clearly demonstrate that the size of the initially added secondary phase has an enormous influence on the pinning behavior of the NEG samples. The $J_c(H_a)$ performance at 77 K for four different particle sizes is shown in Fig. 2. It is evident that the size effect affected $J_c$ value not only at low fields but in the whole field range. This might indicate overlapping of the “large” particle pinning mechanism with that of point-like defects. However, the nominal 70 nm particle size seems to be rather large to effectively contribute to single-
vortex pinning by nanoscopic defects. In order to understand this, we performed microstructure and chemical analyses.

Transmission electron microscopy (TEM) was used to observe microstructure with the aim of clarifying the source of the exceptional magnetic performance of the NEG-123 samples. Fig. 3 shows the TEM images of the sample with the

Fig. 1. Field dependence of critical current density for (Nd₀.₃₃Eu₀.₃₃Gd₀.₃₃)Ba₂Cu₃O₇ sample with 30 mol% Gd-211 refined by ball milling for 0.3, 4 and 8h (200 nm, 70 nm, <70 nm average particle size). All samples were measured at 73, 77, 80, and 90 K, H_a||c-axis.

Fig. 2. Field dependence of the critical current density at 77 K for three samples with the same amount (30 mol%) of the Gd-211 phase of different initial size. The maximum current density was obtained in the sample with the size <70 nm; the record critical current value was 190 kA/cm² at remnant state.

Fig. 3. Transmission electron microscopic image of the NEG-123 sample with 30 mol% Gd-211 refined by ball milling for 4 h (70 nm in size). Note the submicron Gd-211 inclusions and twin planes. The arrows point to the nanometer size Zr-rich NEG–Ba–Cu–O inclusions (top figure). Bottom figures present some selected inclusions of this kind at higher magnification.
Gd-211 particle average starting size of 70 nm, viewed from the (001) direction. One can observe relatively large and irregular particles in size of about 300–500 nm and some tiny particles smaller than 50 nm. In the bottom of Fig. 3 there are three high magnification TEM images of some selected tiny particles. EDX analysis clarified that larger particles are Gd-211 or Gd-rich NEG-211. This result is similar to our previous reports [12]. However, small particles 20–50 nm in size turned out to be Zr-rich NEG–Ba–Cu–O. This new compound was evidently formed during the melt growth and Zr entered the secondary phase during the ball milling process. More details on the chemical composition of these particles can be found in Ref. [15].

Fig. 4 shows the dynamic force microscopy images of the sample with 30 mol% Gd-211 refined by ball milling for 4 and 8 h (the final average size of 70 and <70 nm, respectively), viewed from [001] direction. The most interesting feature of these images was the presence of the particles with sizes from 20 to 50 nm, significantly less than that of the initially added secondary phase. The quantity of these nano-particles increased with ball milling time (cf. Fig. 4 top and bottom).

These TEM and DFM results lead to the conclusion that the Zr-rich NEG–Ba–Cu–O defects are the relevant pinning medium that enhances the magnetic performance at temperatures as high as 90.2 K.

Fig. 4. Dynamic force microscope images of NEG-123 sample with 30 mol% Gd-211 refined by ball milling for 4 h (top figure) and for 8 h (bottom figure). The black arrows point to nano-meter size Zr-rich particles.

Fig. 5. A permanent Fe–Nd–B magnet is stably levitated over an NEG-123 + 30 mol% Gd-211 (average particle size <70 nm) superconductor at liquid oxygen temperature (90.2 K). The superconductor had been magnetized with the permanent magnet and cooled down to 90.2 K (top figure). The bottom figure presents the “permanent” NEG-123 magnet suspended below another NEG-123 superconductor cooled to 90.2 K.
Because of the outstanding increase of the remnant $J_c$ at high temperatures (40 kA/cm$^2$ at 90.2 K), the operating temperature of the superconducting “permanent” magnets shifted from liquid nitrogen (77.3 K) to liquid oxygen temperature (90.2 K). Thus, a levitation experiment could be realized with liquid oxygen cooling, with a permanent magnet suspended over and below the NEG-123 superconductor (Fig. 5). Recently, we succeeded in levitating more than 0.5 kg weight, using two 24 mm NEG-123 bulks cooled by liquid oxygen. The levitation experiment was enabled by a reasonably high trapped field [16]. The trapped field mapping showed that the sample broke during the magnetization process (two peaks of the trapped field) [16]. For practical purposes, the samples will need to be reinforced e.g. by resin impregnation [4] or silver oxide doping [17]. With such treatments our new material can be used in construction of non-contact liquid oxygen pumps for use e.g. in hospitals or in space programs.

4. Summary

The ternary NEG-123 melt-processed material with starting average Gd-211 particle size <70 nm exhibits high $J_c$ up to liquid oxygen temperature. The microstructure study indicates that the improved flux pinning is due to nanometer-size Zr-rich NEG–Ba–Cu–O particles. The experiments at liquid oxygen temperature suggest that the new material can find novel applications such as the construction of non-contact liquid oxygen pumps for medicine and space program.

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References