Strong pinning in ternary (Nd–Sm–Gd)Ba$_2$Cu$_3$O$_y$ superconductors

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We have studied the flux pinning in melt-textured (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ NSG-123 superconductors with various numbers of Gd$_2$BaCuO$_5$ (Gd-211) particles. Transmission electron microscopy (TEM) showed that submicron Gd-211 particles are uniformly distributed in the superconductive matrix. Dark-field TEM observations further showed that a high density of RE rich RE$_{1-$x}Ba$_2$Cu$_3$O$_y$ (RE-123ss) clusters 3–10 nm in size were distributed in the NSG-123 matrix. A strongly developed fishtail was observed in the magnetization hysteresis loops of all the samples. A critical current density of 100 kA/cm$^2$ (77 K) was achieved at the secondary peak field of 2 T for the $H\parallel c$ axis in the NSG-123 sample with 10 mol % Gd-211. Large grain NSG-123 pellets with 30 mol % Gd-211 and 20 wt % Ag$_2$O, 30 mm in diameter and 15 mm in height, exhibited a single-cone profile with a peak value of 1.2 T at 77 K. A higher trapped-field value of 1.5 T was recorded at 2 T, reflecting the secondary peak effect. © 2002 American Institute of Physics.

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A big effort has been made in the last few years to improve the pinning performance as well as the mechanical properties of bulk high-$T_c$ superconductors for various industrial applications. The ability of large-grain REBa$_2$Cu$_3$O$_y$ (RE: rare earth) superconductors to trap magnetic fields much higher than conventional permanent magnets is attractive for high-field applications. Recent advancement in melt-processing techniques, especially in the oxygen-controlled melt-growth (OCMG) process, has allowed the fabrication of single-grain materials with high pinning ability. The trapped magnetic fields in such pellets now meet the requirements of several bulk-type applications at liquid nitrogen temperature. However, further development of the technology is needed for challenging applications like magnetically levitated vehicles (MAGLEVs). Europe, Japan and the United States have already sought to replace low-$T_c$ coils by high-$T_c$ bulk superconducting magnets. Numerical simulations made by the Railway Technical Research Institute clarified that bulk superconductors 10 cm in diameter with critical current density of 100 kA/cm$^2$ at 77 K and magnetic fields of 5 T are required for potential use in MAGLEV systems. (Nd$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$, NEG-123 (Ref. 8), exhibits $J_c$ values higher than those of YBa$_2$Cu$_3$O$_y$ and single-LREEBa$_2$Cu$_3$O$_y$ (LREE=Nd, Sm, Eu, Gd) materials. Our recent results indicate that flux pinning in intermediate fields can be effectively controlled by changing the chemical ratio of Nd:Eu:Gd in the NEG-123 matrix.

In the present study we show that strong flux pinning can be achieved in a ternary (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$, NSG-123 system with a suitable concentration of fine secondary phase particles. High-purity commercial powders of Nd$_2$O$_3$, Sm$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$, and CuO were weighed and determined to have a nominal composition of (Nd$_{0.33}$Sm$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ (NSG-123), then thoroughly ground, calcinated at 880 °C for 24 h with intermediate grinding, and pressed into pellets. The sintering was carried out at 900 °C for 15 h. This whole process was repeated three times under low oxygen partial pressure.

In the second step, commercial high-purity Gd-211 (<1 μm) powders with the volume fractions of 10, 20, 30, and 40 mol % were added to NSG-123. In order to reduce the size of the Gd-211 particles, 0.5 mol % of Pt and 1 mol % CeO$_2$ were added to all the samples. Finally, the product was ground, and pressed into pellets 20 mm in diameter and 15 mm in thickness that were subjected to cold isostatic pressing (CIP) under pressure of 200 MPa. Single-grain NSG-123 samples were grown in a tube furnace using the OCMG process combined with the top-seeded melt-growth technique, details of which were reported in Ref. 12. For oxygenation, small specimens with dimensions of $a \times b \times c = 1.5 \times 1.5 \times 0.4$ mm$^3$ were cut from the as-grown pellets and annealed in flowing O$_2$ gas in the temperature range of 300–600 °C.

The microstructure of these samples was studied by a transmission electron microscope (TEM). The chemical composition of the matrix and of the secondary phase was determined by energy dispersive x-ray (EDX) analysis. $J_c$ values were calculated from magnetization hysteresis loops (MHLs) measured in applied fields up to 7 T by a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, model MPMS7), based on the extended Bean critical state model. The external magnetic field was always applied parallel to the $c$ axis of the sample. For the trapped-field measurements the samples were cooled by liquid nitrogen in magnetic field of 5 T applied parallel to the $c$ axis. The field distribution was then measured by scanning a Hall probe sensor adjusted to 2 mm above the sample surface as the applied field was gradually reduced from 5 to 0 T at 0.5 T step. Details of the measurement procedure were described in Ref. 12.

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The field dependence of the critical current densities of four NSG-123 samples with different Gd-211 contents is presented in Fig. 1. All measurements were performed at $T = 77$ K. A high secondary peak in the $J_c(H_{\parallel}c)$ dependence was observed, and the highest $J_c$ value reached 100 kA/cm$^2$ at 2 T ($H_{\parallel}c$) in the sample with 10 mol % Gd-211. We believe this is the highest value at nonzero field reported so far for melt-processed LRE-123 bulk superconductors. The secondary peak $J_c$ values for the samples with 20, 30, and 40 mol % Gd-211 were 76, 80, and 72 kA/cm$^2$ at respective peak fields of 2.2, 1.6, and 1.6 T. The remanent value of $J_c$ systematically increased with an increase in the Gd-211 concentration. It clearly reflects the role of fine 211 secondary phase particles in low-field pinning. On the other hand, $H_{\text{irr}}$ and the secondary peak positions were relatively low for Gd-211 concentrations of 30 and 40 mol %, mostly due to an improper chemical ratio of the NSG-123 matrix.

In order to study the pinning performance in the NSG-123 samples with 10 and 30 mol % Gd-211 in more detail, we made TEM dark-field observations and the results are presented in Figs. 2(b) and 2(c). The black-and-white contrast reflects the compositional fluctuation induced by RE/Ba substitution. The white region corresponds to the RE-rich area, which was confirmed by TEM-EDX analysis. The size of the RE-rich clusters ranged from 3 to 10 nm, however, they often agglomerate and form larger clusters of around 60 nm. Moreover, the cluster size was different in both samples, which might affect the high-field $J_c(H_{\parallel}c)$ performance. It is well known that the pinning in high fields is mainly governed by point-like pinning disorders that arise from oxygen deficient zones, Ba-rich clusters, and RE–Ba solid solution. However, the present TEM analysis provides evidence that dominant pinning centers in the ternary NSG-123 system is chemical fluctuation in the RE-123 matrix. A comparison with other works is needed to fully understand the pinning mechanism.
FIG. 4. Trapped-field distribution in sample NSG-123 + 30 mol % Gd-211 + 0.5 mol % Pt + 1 mol % CeO$_2$, with 20 wt % Ag$_2$O at 77 K: the remanent state (top part) and with the presence of external field of 2 T (inset of bottom part). Bottom part: External-field dependence of the maximum trapped field. The measurements were performed as the external field was gradually reduced from 5 to 0 T. The diameter of the sample was 30 mm. Note that a trapped field of 1.5 T was achieved at $B'_e$ = 2 T.

The trapped-field distribution is shown in Fig. 3. Compositional variation always takes place when the system with a solid solution solidifies. Particularly in our ternary systems with different ranges of RE–Ba substitution does competitive nucleation naturally generate the scattering in RE–Ba substitution. This is a probable reason for the high pinning in high magnetic fields observed in these materials. Finely dispersed Gd-211 particles can contribute to the pinning enhancement in a low and intermediate field region.

Figure 4 shows the trapped field distribution of the NSG-123 + 30 mol % Gd-211 pellet 30 mm in diameter in the remanent state (upper part) and at an applied field of 2 T (inset in the lower part). Since cracking was often observed during the trapped-field measurements, the amount of Ag$_2$O was increased to 20 wt % for this particular sample in order to improve the mechanical properties. The trapped field exhibits a simple cone profile indicating the absence of extensive cracks in the sample. It also shows that the bulk is a single domain.

Field dependence of the maximum trapped field is shown in the lower part of Fig. 4. We note that the field trapping behavior is basically based on the $J_c(H)$ dependence shown in Fig. 1. When the external field was reduced from 5 to 2 T at 77 K, a trapped field of 1.5 T was achieved. In the remanent state, the trapped field was only 1.2 T. The superior field-trapping capability of this sample in high fields implies that NSG-123 pellets of larger diameter can trap even higher fields.

In summary, submicron Gd-211 particles and matrix chemical fluctuation on a microscopic scale were the dominant pinning centers in NSG-123 samples. A record high $J_c$ value of 100 kA/cm$^2$ at 77 K and 2 T ($H/|c|$) was achieved in the NSG-123 sample with 10 mol % Gd-211. The trapped-field distribution for the NSG-123 pellet containing 30 mol % Gd-211 and 20 wt % of Ag$_2$O exhibited a single cone profile with the peak value of 1.5 T at 77 K and 2 T. The high $J_c$ and high-field-trapping capability of this sample in high magnetic fields of this NSG-123 system imply a significant potential of the material for high-field applications.

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