High-$T_c$ Superconducting Magnets That Function at Liquid Oxygen Temperature

M. Muralidhar, N. Sakai, M. Jirsa, M. Murakami, and N. Koshizuka

Abstract—This article reports on a novel superconducting material suitable for a superconducting magnet that can function up to liquid oxygen temperature (90.2 K). This achievement provides a distinguished step toward industrial applications of liquid oxygen, which is as broad as those of liquid nitrogen. The strong flux pinning at 90.2 K was recently achieved in a $(\text{Nd}_{0.33}\text{Eu}_{0.33}\text{Gd}_{0.33})\text{Ba}_2\text{Cu}_3\text{O}_y$ compound in that nanometer size Zr-based pinning centers are distributed. This composite exhibited at 90.2 K an outstanding critical current density $>40\ \text{kA/cm}^2$ that fulfills requirements of some industrial applications.

Index Terms—Critical current density, flux pinning, melt-processed bulk materials, superconducting magnets at 90.2 K.

I. INTRODUCTION

RECENT progress in the fabrication technology of melt-textured REBa$_2$Cu$_3$O$_y$ "RE-123" high-$T_c$ superconductors has enabled the applications of superconducting permanent magnets. Most applications of superconducting bulk magnets like magnetic separators, magnetron sputtering, and transport systems have been available only at or below the boiling point of liquid nitrogen [1]–[5]. Such applications require a good vortex pinning performance and the associated high critical current density. In an attempt to improve the pinning performance at high temperatures, we developed ternary LREBa$_2$Cu$_3$O$_y$ "LRE-123" (LRE = light rare earth, LRE = La, Nd, Eu, Sm, Gd) materials and succeeded in preparing the disks several centimeters in diameter [6], [7]. In the previous report, we described how the pinning performance could be controlled in the LRE-123 systems [8]. The systematic study of the ternary $(\text{Nd},\text{Eu},\text{Gd})\text{Ba}_2\text{Cu}_3\text{O}_y$ "NEG-123" system revealed that control of the Nd: Eu: Gd ratio in the NEG-123 matrix enabled us to tailor the pinning performance according to the requirements of the specific use. One can produce materials with a high narrow secondary peak of $J_c(B)$ at moderate fields or with a rather broad moderate peak with maximum at fields as high as 4 T (77 K) [9]. A choice of the Nd: Eu: Gd ratio made it possible to control the secondary peak field between 1 and 4 T at 77 K. In a certain range of Nd: Eu: Gd ratio, an ordered variation in the NEG-123 matrix composition appeared, which enhanced vortex pinning up to exceptionally high fields [10]. On the other hand, externally added secondary phase particles to melt-textured materials enhance critical current density at low fields [8]. With the aid of further improving low-field pinning performance, we reduced the size of the initially added secondary phase particles, since their efficiency is inversely proportional to their size [11]. The refinement of Gd$_2$BaCuO$_y$ "Gd-211" particles to tens of nanometers was performed by ball-milling the powder by Y$_2$O$_3$ – ZrO$_2$ balls. This treatment created new nano-scale Zr-rich NEG-Ba-Cu-O precipitates, accompanied by an exceptional pinning enhancement not only at 77 K but also up to much higher temperatures, close to $T_c$. As a result, this material showed very high critical current density at 90.2 K, the boiling temperature of liquid oxygen [12]. Using this material, we could levitation a permanent magnet at 90.2 K.

In this paper, we present the results of microstructure, magnetization, and trapped field measurements and discuss the size effect of initially added Gd-211 secondary phase, especially from the viewpoint of the applications of a superconducting permanent magnet with liquid oxygen refrigeration.

II. EXPERIMENT

High-purity commercial powders of Nd$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, BaCO$_3$, and CuO were mixed in quantities corresponding to a nominal composition of $(\text{Nd}_{0.33}\text{Eu}_{0.33}\text{Gd}_{0.33})\text{Ba}_2\text{Cu}_3\text{O}_y$. The starting powders were thoroughly ground and calcined at 880°C for 24 h with intermediate grinding, then pressed into pellets. Sintering was carried out at 900°C for 15 h. This process was repeated three times under oxygen partial pressure (pO$_2$) of 1% O$_2$.

In the second step, the powders of Gd$_2$O$_3$, BaO, and CuO were mixed to have a nominal composition of Gd$_2$BaCuO$_y$ and calcined twice at 840 and 900°C for 4 h. The calcined Gd-211 powders were milled using Y$_2$O$_3$ – ZrO$_2$ balls in acetone for 0.3–8 h. The average size of the ball-milled powders was 200 to less than 70 nm after 0.3–8 h milling, as confirmed by Brunauer-Emmett-Teller (BET) specific area measurements [13]. 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 the melting, 0.5 mol% Pt and 1 mol% CeO$_2$ were added. The powder mixture was pressed into pellets of 20 mm diameter and subjected to cold isostatic pressing under 200 MPa. Finally, a MgO (100) seed was placed at the top center of the pellet, which was then melt-grown in the
Melt processed Y-123 samples did not exhibit the secondary peak effect (at 77 K) and the irreversibility field was around 4 T. The Nd-123 sample showed a well developed secondary peak located at 2 T but relatively low remnant $J_c$. On the other hand, remnant $J_c$ dramatically increased in NEG-123 samples with decreasing the size of initially added Gd-211 particles. Fig. 1 clearly demonstrates superiority of NEG-123 composites among other members of the RE-123 family.

The Gd-211 particle average starting size of <70 nm was achieved after ball milling for 8 h and the sample with 30 mol% of this powder exhibited at 77 K the remnant $J_c$ over 190 kA/cm². A similar value was also obtained in the sample with 40 mol% Gd-211 ball-milled for 4 h [12]. The effect of the particle size reduction on remnant $J_c$ was expected as it corresponded to the theoretically predicted dependence. However, critical current density at moderate fields also increased with increasing ball-milling time. This is not so easy to explain as the 211 particles of about 70 nm size are still too large to act as point-like defects that are known as being responsible for the secondary peak. In order to clarify this, we performed microstructure and chemical analysis.

### B. Microstructure Analysis

To understand the improved magnetic performance, we studied the microstructure of the (Nd₀.₃₃Eu₀.₃₃Gd₀.₃₃)Ba₂Cu₄O₈ samples using transmission electron microscopy (TEM) and dynamic force microscopy (DFM). We found new particles 20 to 50 nm in size were uniformly dispersed in the 123 matrix [17]. The energy dispersive X-ray analysis clarified that these particles consisted of 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 [17].

The dispersion of the small nano-particles in the superconducting matrix explains the enormous rise of $J_c$ shown in Fig. 1, not only at zero field but also at intermediate fields. However, $J_c$ was enhanced not only at 77 K but also significantly increased even above 90 K. The sample with 40 mol% of Gd-211 particles with the average size 70 nm showed at 90 K the remnant $J_c$ around 40 kA/cm² [12].

### C. Trapped Field Experiments

Trapped-field measurements of NEG-123 disks were performed at liquid nitrogen temperature (77.3 K) and liquid oxygen temperature (90.2 K). First, the samples were cooled by liquid nitrogen in magnetic field of 2 T applied parallel to the c-axis. The field distribution was then measured by a Hall probe sensor scanned at 1.2 mm above the sample surface, in the remnant state. The same procedure was used for the measurements at liquid oxygen temperature. Fig. 2 shows trapped-field for the NEG-123 sample with 30 mol% Gd-211 refined by ball milling for 4 hours. The sample size was 16 mm in diameter and 6 mm in thickness.

A single cone profile with the peak value of 0.5 T at 77 K and zero field was observed. In this case, the sample was thin, therefore it was difficult to compare the trapped field data with thicker.
Fig. 2. The trapped field distribution in the sample NEG - 123 + 30 mol% Gd - 211 (70 nm in size), melt processed in Ar-1% O₂, at liquid nitrogen temperature. The diameter of the sample was 16 mm and 6 mm in thickness. Trapped field of 0.5 T was achieved in the remanent state.

Fig. 3. The trapped field distribution in the sample NEG - 123 + 40 mol% Gd - 211 (70 nm in size), melt processed in Ar-1% O₂, at liquid oxygen temperature. The sample had 24 mm in diameter and was 12 mm thick. The trapped field of 0.16 T was achieved in the remanent state.

Fig. 4. (a) Permanent Fe-Nd-B magnet floats above an NEG - 123 + 40 mol% Gd - 211 (70 nm in size) superconductor at liquid oxygen temperature (90.2 K), after the superconductor had been magnetized by stray field of the permanent magnet and cooled down to 90.2 K; (b) the same with a tilted Fe-Nd-B magnet. Liquid oxygen is attracted to the magnet due to its paramagnetism.

D. Levitation Experiments at 90.2 K

Several years after the discovery of high temperature superconductivity, we developed a NEG-123 disk capable of levitation with liquid oxygen cooling (Fig. 4(a)). Using the new NEG-123 superconductor with nanometer size secondary phase precipitates combined with super-small Zr-rich particles, one can levitate a heavily loaded permanent magnet at 90.2 K as shown in Fig. 4(b). As liquid oxygen is paramagnetic, it is attracted to a magnetized bulk material. Alternatively, the permanent magnet can be suspended below the superconductor [12]. The same experiments were also performed with two superconducting magnets. The new superconducting magnet behaves at liquid oxygen (90.2 K) exactly like a YBa₂Cu₃O₇₉ disk at liquid nitrogen (77.3 K) [1]. The levitation experiments proved that the new material enables the construction of noncontact pumps for transport of liquid gases including liquid oxygen. Thus, our latest results represent a significant step of bulk high-T_c superconductors toward novel engineering applications.

IV. Summary

The ternary melt-processed NEG-123 with 30 mol% of Gd-211 ball milled down to the average initial particle size of <70 nm exhibited respective critical current densities of 190 and 100 kA/cm² at zero and 3 T at 77 K (H ∥ c-axis). It also showed remnant J_c > 40 kA/cm² at 90 K. The dynamic force
microscopy observations showed that excellent flux pinning at 90 K is due to a combination of small secondary phase precipitates combined with Zr-rich NEG-Ba-Cu-O particles of only a few tens of nanometers in size. The trapped field experiments at 90.2 K demonstrated that the new material has significant potential for new applications with liquid oxygen cooling.

REFERENCES


