Enhanced Superconducting Properties in Melt-processed $(Y_{0.33}Sm_{0.33}Nd_{0.33})$ $Ba_2Cu_3O_y$ Oxides in Air

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We have systematically studied the superconducting properties and flux pinning enhancement of $(Y_{0.33}Sm_{0.33}Nd_{0.33})Ba_2Cu_3O_y$ [(YSN)-123] composite oxides by melt growth process in air. A sample prepared by this method showed well-textured microstructure, and $(Y_{0.33}Sm_{0.33}Nd_{0.33})_2BaCuO_5$ [(YSN)211] nonsuperconducting particles were uniformly dispersed in large (YSN)123 superconducting matrix. The sample showed a sharp superconducting transition at 91 K. The magnetization measurements of the (YSN)-123 sample exhibited the enhanced flux pinning, compared with $YBa_2Cu_3O_y$ (Y-123) sample without Sm and Nd. Critical current densities of (YSN)-123 sample was 2.5×10^4 A/cm^2 at 2 T and 77 K.

Keywords : (YSN)-123, Melt growth process, Flux pinning, (YSN)211, Critical current density

1. INTRODUCTION

For large-scale applications of high T_c superconductors, large monolithic superconducting materials are required. Such materials are most favorably grown by the melt processing route. Rare earth(RE: Nd, Sm, etc.) compounds are being used in a large variety of practical applications such as permanent magnet, flywheels, fault current limiters, magneto-optical recording disks, chemical sensors, etc. In order to achieve a large critical current density in a magnetic field, it is necessary to introduce strong pinning centers into the superconductors. In bulk YBCO compound, however, critical current densities are limited by weak links between grain boundaries. Melt-textured growth(MTG) process of the REBCO superconductor is a good fabrication method to eliminate the weak links and obtain large grain with good alignment so as to increase critical current density directly or indirectly[1-4]. Additionally, the melt-textured high T_c superconductor enables flux pinning to improve by introducing fine dispersion of second phase precipitate, such as Y_2BaCuO_5(Y211), which acts as pinning center. The OCMG(oxygen-controlled melt-growth)-processed REBCO superconductors have been reported to increase T_c(K) and critical current density(J_c)[2,5]. It is remarkable that flux pinning of melt-textured REBCO is larger than that of melt textured YBCO in high field region. These systems are characterized by a solid solution between the RE and Ba atoms. Thus, under normal preparation conditions in air, the superconductivity is partially suppressed. By means of the OCMG process, it has some drawbacks, including additional cost and equipment for commercialization. To objective of this study is to investigate the method of enhancing superconducting properties in air through the complete substitution of the RE and Y composite oxides.

In this paper we report on the analysis of microstructure magnetization measurements, critical current densities and improved flux pinning properties of (YSN)-123 oxides prepared by melt-textured growth process in air.

2. EXPERIMENTAL

Melt growth process for fabricating (YSN)-123 superconductor containing (YSN)211 second phase is as follows. Precursor powders prepared from raw materials of Y_2O_3, Sm_2O_3, Nd_2O_3, $BaCO_3$, and CuO powders were mixed for a nominal composition of (YSN)-123. The

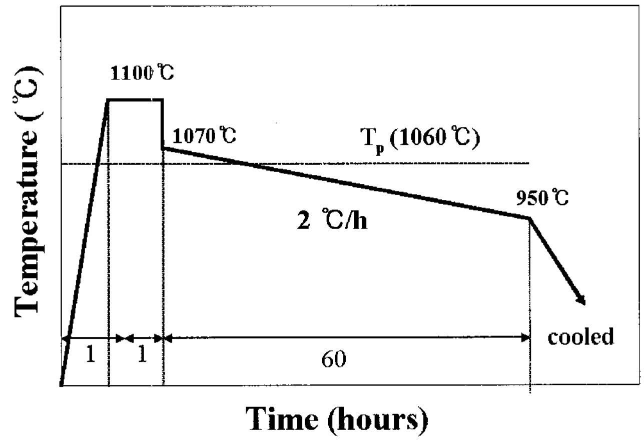

Fig. 1. Temperature profile for the fabrication of the (YSN)-123 bulk sample.

sub-micron sized (YSN)211 particles were prepared by QMG(quench and melt growth) method at 1200 °C with Pt crucible. The mixed powders with 30 mol.% (YSN)211 particles calcined at 900 °C for 24 h twice in air with intermediate grinding. The calcined powders with 1 wt.% CeO_2 were milled with attrition for 6 h in acetone using zirconia balls with a rotation speed 450 rpm. The (YSN)-123 powders milled with attrition were dried in air, and then pressed into pellets 10 mm in diameter and 5 mm in thickness, which were then subjected to a cold isostatic press, CIP, treatment with a pressure of 200 MPa. The pressed samples were melt-textured in a box furnace in nominal air atmosphere[4]. A (001) MgO single crystal was used as the substrate.

The heat treatment profile(as shown in Fig. 1) used in the present experiment was as follows. The sample was heated to temperature 1110 °C (peritectic temperature, T_P: 1060 °C in air) in 1 h and held for 1 h, then rapidly cooled 1070 °C in 5 min, and slowly cooled by 950 °C with a cooling rate of 2 °C/h. Finally, they were furnace cooled to room temperature.

The post-heat treatment was performed at 450 °C oxygen gas atmosphere for 100 h in a tube furnace. The melt-textured growth (YSN)-123 sample with a single domain was split into several platelets with thickness 0.5-1 mm from the cleaved plane for characterization. The microstructure of the sample was characterized by TEM. For analyzing the pinning effect, magnetization hysteresis of the samples were measured for H//c-axis in a SQUID magnetometer(Quantum Design MPMS-7) at various temperature from 10 K to 85 K. J_c values were estimated according to the extended Bean's formula[6] using the following equation $J_c = 20(\Delta M)/[a(1-a/3b)]$, where ΔM is the difference in magnetization between increasing and decreasing magnetic fields and a and b are sample dimension for a rectangular shape.

3. RESULTS AND DISCUSSION

Critical current densities in high T_c bulk superconductors depend closely on the microstructure of the material. In the REBCO system, crystal defects of different kinds such as 211 precipitates, oxygen vacancies, twin boundaries, dislocations, microcracks etc., are present in the RE123 matrix that can act as effective pinning centers[2,7-10]. In addition to the crystal defects, fine dispersion of RE211 inclusions are known to be effective in enhancing flux pinning at 77 K. The smaller size of these particles, the more effective flux pinning site is on them. The melt-textured YBCO and REBCO systems exhibits enhancing flux pinning effect because 211 inclusions dispersed in 123 matrix work as pinning centers[7,11]. Therefore, control of the size and morphology of defect structure is essential for the fabrication of the superconducting material with high pinning efficiency. Figure 2 shows optical micrograph of the melt-textured (YSN)-123 crystal. It can be seen in Fig. 2 that the uniform (YSN)211 inclusions are trapped within the (YSN)123 matrix. The (YSN)211 inclusions have spherical shape. This refinement of (YSN)211 inclusions is observed for all samples. This result is attributed to, in part, the finely dispersive (YSN)211 inclusions which apparently act as effective pinning centers.

In order to obtain more detailed information about the size and the chemical composition of the (YSN)123 matrix and (YSN)211 inclusions, we performed TEM observations in conjunction with energy dispersive X-ray spectroscopy(EDS) analyses. TEM samples are prepared both by ion milling and mechanical crushing to avoid the artifacts due to the sample preparation. Figure 3 shows TEM bright image around the (YSN)211 particle and selected area electron diffraction(SAED) pattern of the (YSN)123 matrix viewed from a [001] direction. In Table 1, TEM-EDS analyses of (YSN)123 matrix and (YSN)211 inclusion shown in Fig. 3 was presented that (YSN)123 matrix and (YSN)211 inclusions contain Y, Sm, and Nd with an even ratio, which are identical to the nominal composition of the precursor powders, that are, (YSN)123 and (YSN)211.

In order to find out how the sample consists of superconducting phase, magnetic susceptibility of the melt-textured (YSN)-123 sample was measured. The field of 1 mT was applied parallel to the c-axis from 10

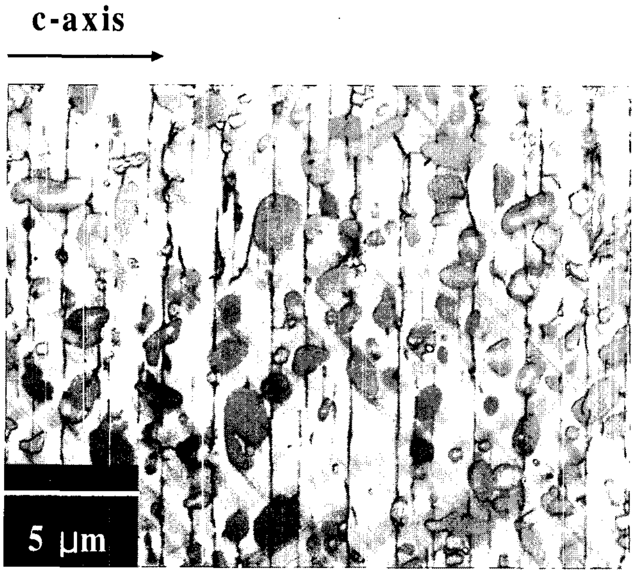

Fig. 2. Optical micrograph of the melt-textured (YSN)-123 crystal. Note finely dispersed (YSN)211 inclusions are trapped within the (YSN) matrix.

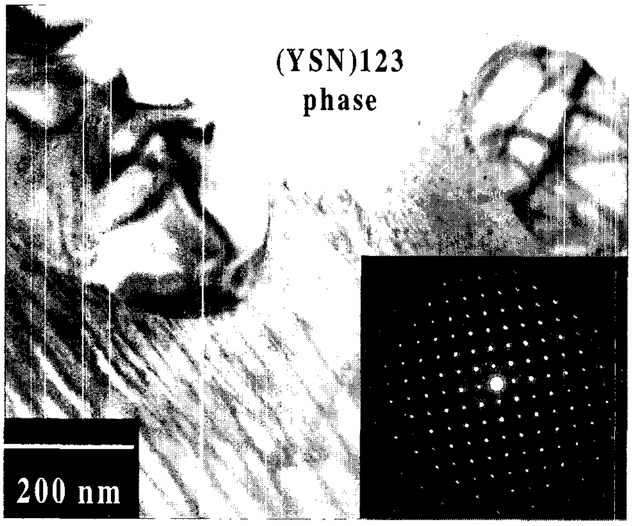

Fig. 3. TEM image and SAED pattern of the melt-textured (YSN)-123 sample. (YSN)211 inclusions and dense twin patterns are seen in the image.

Table 1. TEM-EDS analysis on (YSN)123 matrix and (YSN)211 inclusion of as grown (YSN)-123 crystal shown in Fig. 3.

Element(at%)	(YSN)123 matrix	(YSN)211 inclusion
Y	2.887	6.802
Sm	2.895	7.105
Nd	2.785	7.215
Ba	18.562	11.016
Cu	26.853	10.793

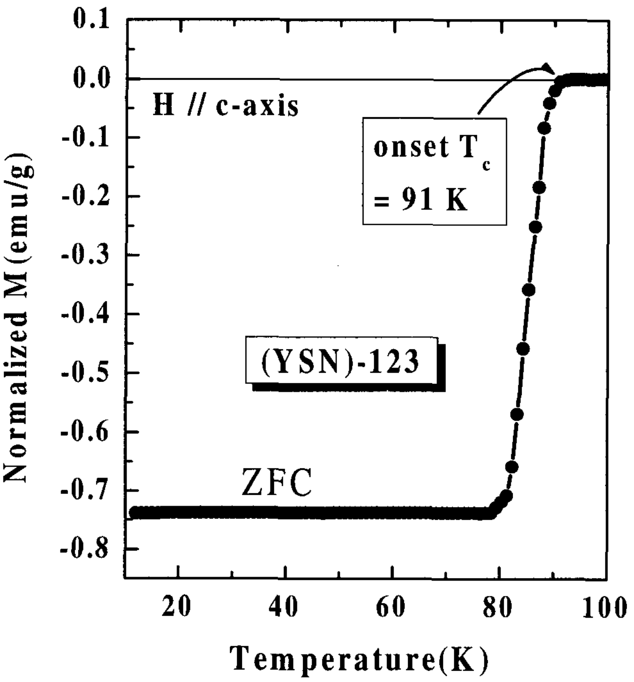

Fig. 4. Temperature dependence of magnetic susceptibility of the melt-textured (YSN)-123 sample.

to 100 K. As shown in Fig. 4, the (YSN)-123 sample shows a sharp superconducting transition at 91 K, indicating that the sample consists of a homogeneous superconducting phase.

For the analysis of flux pinning, magnetization hysteresis loops of (YSN)-123 and Y-123 samples were measured from 10 to 85 K as a function of the magnetic field(//c-axis) up to 2 T. Among the hysteresis results, a representative hysteresis loop at 50 K is shown in Fig. 5. The (YSN)-123 sample shows about 5 times larger magnetization hysteresis loop than that of melt-textured Y-123 sample at 2 tesla. To increase pinning effect, total area of the interface should be important ; smaller Y211 inclusions are more efficient in enhancing flux pinning. It is reported that the melt-textured YBCO, fabricated by TSMG(top-seeded melt growth) method, exhibits enormous magnetic hysteresis loop because finely dispersed Y211 particles in Y123 matrix work as pinning centers[11].

The pinning effect in REBCO (OCMG) is larger than that in YBCO, indicating that the superconducting

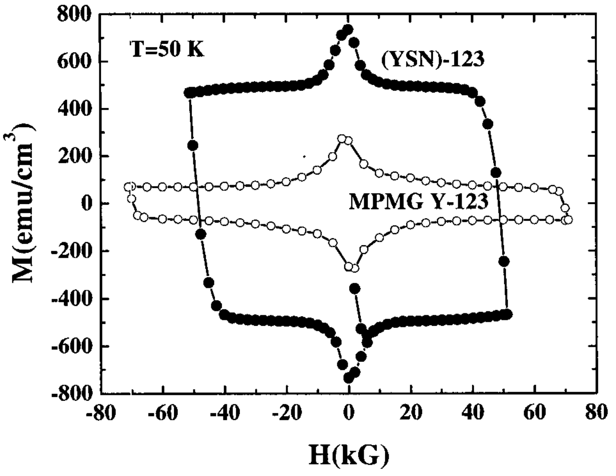

Fig. 5. Magnetization hysteresis loops of the melt-textured (YSN)-123 sample. The melt-textured (YSN)-123 sample shows about 5 times larger magnetization hysteresis loop than that of MPMG Y-123 sample at 5 T.

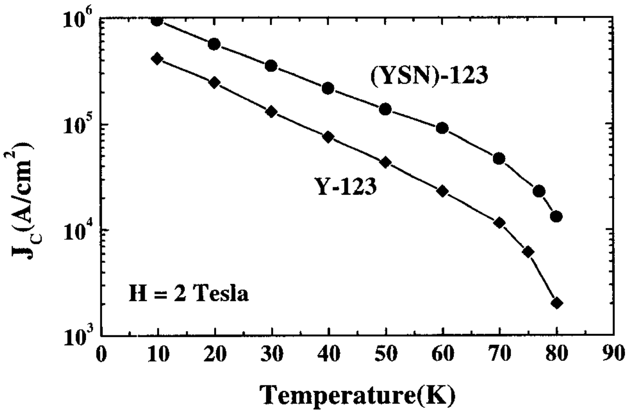

Fig. 6. Field dependence of critical current densities of the melt-textured (YSN)-123 sample at various temperatures.

(YSN)123 phase in our (YSN)-123 sample may have enhanced pining effect as well. The sharp interface as well as the substitution of RE for of Y in (YSN)-123 compound may provide more effective pinning centers than in Y-123 samples.

The critical current densities of the (YSN)-123 sample derived from the magnetization hysteresis loops at various temperatures are shown in Fig. 6. As illustrated in Fig. 5, the field dependence of critical current densities rapidly decreases with increasing of applied fields at 77 K, while it does not change that much at 60 K regions. The critical current density J_c of our sample is calculated at 2 T and 77 K. The value of J_c is 2.5×10^4 A/cm^2, which is higher than that($\approx5{,}000$ A/cm^2)of Y-123 sample. The high J_c value at zero-field in (YSN)-123 system may originate from the sub-micron sized fine (YSN)211 particles.

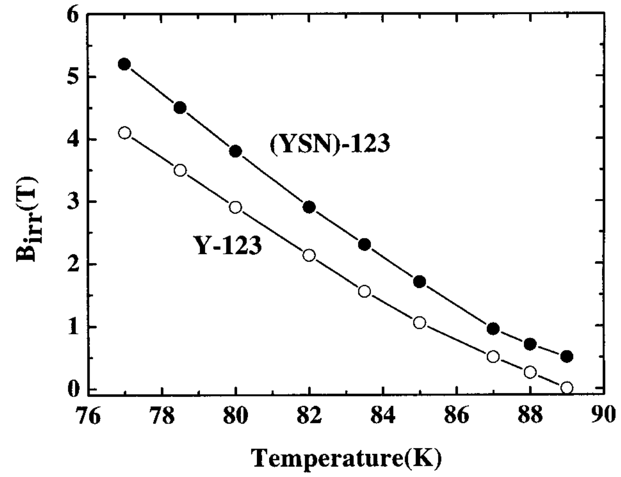

Fig. 7. Temperature(K) dependence of irreversibility field(T).

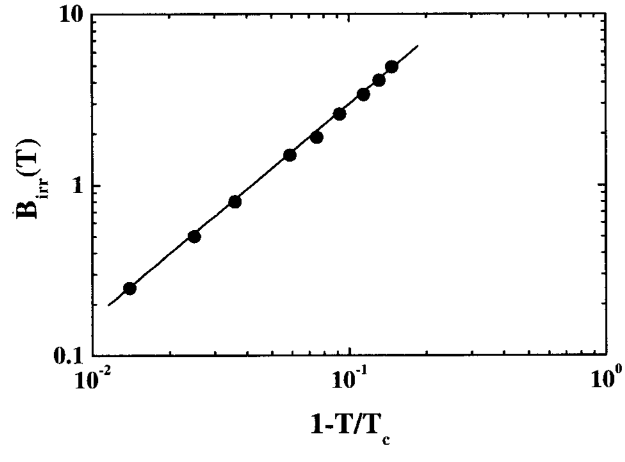

Fig. 8. Irreversibility field with reduced temperature of the melt-textured (YSN)-123 sample.

For a comparison of the pinning strength between different high T_c superconductors, a simultaneous location of their irreversibility lines in the field-temperature(H-T) has been useful. Irreversibility line defines a boundary in the H-T phase diagram above which J_c is immeasurably small or zero. Zero resistance state is only achieved in pinned or irreversible high T_c superconductors, in which flux motion is prevented by pinning centers against the electromagnetic force. Figure 7 shows temperature dependence of the irreversibility field with H//c-axis for (YSN)-123 and Y-123 samples. As shown in Fig. 7, the (YSN)-123 sample shows higher irreversibility field than that of Y-123. This result, it seems that the flux pinning mechanism by the finer (YSN)211 addition within the (YSN)123 matrix is more effective in improving J_c of the (YSN)-123 sample than the coarse (YNS)211 dispersion.

Since high T_c superconductors cannot be used beyond this line, it is desirable that the materials have high enough irreversibility field at a temperature where they are used. According to the collective flux creep theory[12], the irreversibility field B_{irr} is given by $B_{irr} \propto [1-(T/T_c)^2]^{1.5}$. Several techniques are used in determining the irreversibility field. In this paper, we have adopted the DC magnetization method by SQUID magnetometer.

Figure 8 shows the irreversibility field(B_{irr}) versus reduced temperature $[1-(T/T_c)]$ on logarithmic scales for the (YSN)-123 sample. From least square fit of the data, $n \cong 1.5$ was calculated. This means that the temperature dependence of irreversibility line is close to YBCO (n=1.5), and the irreversibility fields(B_{irr}) shows a slight change in low and high temperature regions.

4. CONCLUSION

In summary, we have succeeded in the syntheses of melt-textured (YSN)-123 oxides by MTG process in air. The (YSN)211 inclusions, having spherical shape, are uniformly dispersed within (YSN)123 matrix. The (YSN)-123 sample as a transition temperature of 91 K consists of homogeneous superconducting phase. The sample shows a larger hysteresis loop than other Y-123 superconductors. Enhanced superconducting properties associated with the refined (YSN)211 inclusion within (YSN)123 matrix and the substitution of RE for Y site in (YSN)-123 oxides. This result would be useful for the application fields of the high T_c bulk superconductors that require large critical current even at high magnetic field.

REFERENCES

[1] S. Jin, T. H. Tiefel, R. C. Sherwood, M. E. Davis, R. B.van Dover, G. W. Kammlott, R. A. Fastnacht, and H. D. Keith, "High critical current in Y-Ba-Cu-O superconductors", Appl. Phys. Lett., Vol. 52, No. 24, p. 2074, 1988.

[2] M. Muralidhar, M. Jirsa, N. Sakai, and M. Murakami, "Progress in melt-processed (Nd-Sm-Gd)$Ba_2Cu_3O_y$ superconductors", Supercond. Sci. Technol., Vol. 16, p. R1. 2003.

[3] F. Giovannelli, A. Ubaldini, and I. Monot-Laffez, "Properties of the $(Sm_{0.33}EU_{0.33}Gd_{0.33})Ba_2Cu_3O_y$ superconductor prepared by different processes in air", Supercond. Sci. Technol., Vol. 16, p. 444, 2003.

[4] S. J. Kim, "Melt textured growth and superconducting properties of RE^{3+} elements doped YBCO superconductors", J. of KIEEME(in Korean) Vol. 16, No. 3, p. 231, 2003.

[5] M. Murakami, S. I. Yoo, T. Higuchi, N. Sakai, M. Watanabiki, N. Koshizuka, and S. Tanaka, "A new type of pinning center in melt grown Nd123 and Sm123", Physica C, Vol. 235, p. 2781, 1994.

[6] E. M. Gyory, R. B. van Dover, K. A. Jacson, L. F. Schneemeyer, and J. V. Waszczak, "Anisotropic critical currents in $Ba_2YCu_3O_7$ analyzed using an extended Bean model", Appl. Phys. Lett., Vol. 55, No. 3, p. 283, 1989.

[7] R. Cloots, T. Koutzarova, J-P. Mathieu, and M. Ausloos, "From RE-211 to RE-123. How to control the final microstructure of superconducting single-domains", Supercond. Sci. Technol., Vol. 18, p. R9, 2005.

[8] S. J. Kim, K. W. Lee, and H. G. Kim, "Characterization and superconducting properties of (Sm/Y)-Ba-Cu-O composite oxides by top-seeded melt growth in air", J. Crystal Growth, Vol. 204, p. 78, 1999.

[9] C. J. Kim, K. B. Kim, H. W. Park, T. H. S, I. H. Kuk, and G. W. Hong, "Microstructure of melt-textured Y-Ba-Cu-O oxides with CeO_2 addition and the formation mechanism of the Ba-Cu-O platelet structure", Supercond. Sci. Technol., Vol. 9, p. 76, 1996.

[10] S. J. Kim, "Flux pinning enhancement and irreversibility line of Sm doped YBCO superconductor by zone melt growth process", Trans. EEM, Vol. 5, p. 81, 2004.

[11] S. Nariki, N. Sakai, M. Murakami, and I. Hirabayashi, "High critical current density in Y-Ba-Cu-O bulk superconductors with very fine Y211 particles", Supercond. Sci. Technol., Vol. 17, p. S30, 2004.

[12] N. Ihara and T. Matsushita, "Effect of flux creep on irreversibility lines in superconductors", Physica C, Vol. 257, p. 223, 1996.