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著者	渡辺　和雄
journal or publication title	IEEE Transactions on Applied Superconductivity
volume	19
number	3
page range	2953-2956
year	2009
URL	http://hdl.handle.net/10097/47199

doi: 10.1109/TASC.2009.2019138

Fabrication and Superconducting Properties of Aluminum Doped (Nd,Sm,Gd)–Ba–Cu–O Filaments

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***Abstract*—$(Nd_{0.33}Sm_{0.33}Gd_{0.33})_{1.18}Ba_{2.12}Cu_{3.09}O_y$ (NSG123) precursor filaments doped with Al were prepared by a solution spinning method and partially melted at 1050°C for 30 min in flowing 0.1% $O_2 + Ar$ gas. Samples were cooled at various rate of 10–60°C/h, and then oxygenated in pure O_2 gas. It was found that the microstructural and superconducting properties were strongly influenced on the cooling rate from partial melting temperature to 900°C during OCMG processing. Although the sample without Al cooled at 20–50°C/h showed J_c value higher than 2.0×10^4 A/cm^2 at 77 K and 0 T, the sample treated at fast cooling rate of 60°C/h exhibited the J_c value of about 3.0×10^3 A/cm^2 at most. In contrast, the NSG123 doped with 0.05at%Al even at a rate of 60°C/h cooling showed high J_c value of 1.5×10^4 A/cm^2 at 77 K and 0 T, and exhibited a well aligned texture and a dense microstructure. From J_c measurements in applied magnetic fields, a J_c value higher than 10^3 A/cm^2 was maintained up to 9 T for 0.05 at% Al doped filament. It was found that a small amount of Al doping into NSG123 was effective on refinement of the size of the NSG211 particle and reduction pores and cracks in microstructure for sample treated even at fast cooling, and thereby increased J_c values.**

***Index Terms*—Al chemical doping, critical current density, magnetic field behavior, (Nd,Sm,Gd)–Ba–Cu–O filament.**

I. Introduction

A long length and a high critical current density (J_c) at 77 K are required to use $REBa_2Cu_3O_{7-\delta}$(RE; Rare Earth, RE123) wires and tapes for practical applications, such as superconducting magnets with high trapped field, flywheels for energy storage and current lead materials. A higher J_c value even in high magnetic fields is favorable for better performance and a safety margin. It is well known that the introduction of artificial pinning centers such as nano-size impurities and metal oxides is one of the most useful techniques to enhance the magnetic flux pinning and the J_c. For this purpose, superconducting coated conductors [1], [2] and wires [3] as well as bulks have been intently studied by many researchers. It has also been found that additions such as Pt, Sn, Zr, Ce and Ti are effective in reducing the size of RE211 inclusion and thereby increasing J_c values [4]–[9]. Recently, Azzouz *et al.* reported that the effect of nano-size Al_2O_3 addition on J_c behaviors and the microstructure for Y123 bulks [10]. However, technical difficulties arise in the area of the artificial defect introduction into RE123 matrix, due to a balance between the enhancement of pinning strength and the degradation of the superconductivity. It is important to control both the size and the distribution of the impurities for optimum flux pinning and enhancement of J_c value. Furthermore, most of RE123 bulk sample preparation needs extremely slow cooling from melting to solidification temperature in order to promote the crystal growth and avoid coarsening of the RE211.

A solution spinning method is one of the chemical routes used in the fabrication of superconducting filaments [11]. This method has the following advantages for fabricating a filamentary sample; a fine filament of desired diameter less than 100 μm with a relatively long length is fabricated in a short time. It is possible to prepare uniform precursor filament without stoichiometric deviation from the starting compositional ratio. There is still another advantage of a simple and inexpensive non-vacuum technique to prepare filamentary superconductor. However, the effect of doping on the superconducting properties for fine filament type LRE123 superconductor has not yet been widely investigated except for a few experiments [3]. Therefore, further studies for high quality LRE123 filament doped with additional impurities are needed to establish the fundamental data and to enhance the superconducting properties.

In this study, we report the effect of Al chemical doping on the microstructure and superconducting properties of fine NSG123 filaments prepared by a short time process via a chemical route.

II. Experimental Procedure

Filamentary superconducting samples were fabricated by a solution spinning method. The precursor NSG123 filament with the starting composition of $Nd_{0.33}Sm_{0.33}Gd_{0.33} : Ba : Cu = 1.18 : 2.12 : 3.09$ was synthesized from a homogeneous aqueous solution containing metal acetates of Nd, Sm, Gd, Ba and Cu, poly(vinyl alcohol), and organic acid. Different amounts of Al ranging from 0 to 0.1 at% using $Al_2O(CH_3COO)_4 . 4H_2O$ relative to Gd123 were also added into an aqueous solution, and thoroughly mixed. After condensation to obtain a stable viscous homogeneous spinning dope, the dope was extruded through the stainless nozzle as a filament shape into a hot air zone, and coiled onto a winding drum. The pyrolysis of the as-drawn filament with 150–200 μm in diameter was carried out to remove extra components such as CO_2. Samples were partially melted at temperature 1050 °C for 30 min partially melted in flowing 0.1% $O_2 + Ar$ gas, and then the samples were cooled in two steps, first cooling step

Manuscript received August 25, 2008. First published June 30, 2009; current version published July 15, 2009.

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Digital Object Identifier 10.1109/TASC.2009.2019138

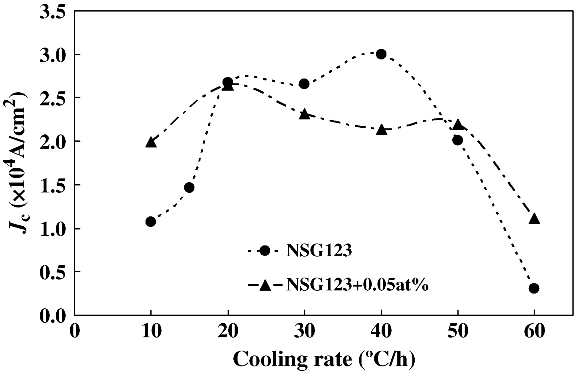

Fig. 1. Transport Jc at 77 K and self-field as a function of cooling rate from partial-melting temperature to 900°C for filamentary NSG123 samples.

from partial-melting temperature to 900 °C was at a various rate of 20 °C/h–60 °C/h and second step from 900 °C to 500 °C was at a rate of 50 °C/h. The oxygenation was finally carried out in flowing pure O_2 gas. Further details of the sample preparation are shown in [3], [12]. After heat treatment, the diameter and the length of the filament samples were about 80–100 μm and 100 mm.

The T_c and transport J_c were measured by a standard DC four-probe resistive method. After cut the sample into pieces with 10 mm in length for measurement, silver paint was used to connect the silver sputtered parts of the sample to Ag electrodes of 100 μm in diameter for supplying DC currents and Ag electrodes of 75 μm in diameter for voltage leads. The sample was embedded on the substrate at the arbitrary direction for the sample diameter using epoxy resin and mounted on a critical-current-measuring holder. The external magnetic field was always applied in a direction perpendicular to the filament length using a high homogeneous 18 T superconducting magnet at the High Field Laboratory for Superconducting Materials, Tohoku University. Current was passed along the direction of the filament length and perpendicular to the applied magnetic field. The J_c was defined by the offset method from the point on the I–V curve at which the voltage of 1 μV appeared between voltage terminals separated by 2 mm. The crystal phases and the microstructure of samples was also studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX).

III. Results and Discussion

Fig. 1 shows transport J_c at 77 K and self-field as a function of cooling rate from 1050 °C to 900 °C. The J_c values of the filamentary sample are found to be dependent on the cooling rate and high J_c values larger than 10^4 A/cm^2 are obtained over a wide cooling rate range of 10 °C/h–50 °C/h. However, the J_c value of NSG123 without Al sample cooled at fast cooling of 60 °C/h is drastically decreased.

Table I summarizes the transport J_c value at 77 K and self-field, T_c, transition width ΔT_c and electrical resistivity at 100 K of three kinds of NSG123 samples processed at various cooling rate. When the sample cooled at a rate of 60°C/h, significant difference in J_c value between NSG123 without Al and Al doped sample can be seen. ΔT_c and electrical resistivity

TABLE I
Superconducting and Electrical Properties of Filamentary Samples

sample	Cooling rate (°C/h)	J_c (A/cm^2)	T_c (K)	ΔT_c (K)	ρ (mΩ·cm)
NSG123	20	26,800	91.3	0.8	0.08
	40	30,000	92.3	1.3	0.30
	60	3,100	91.8	2.2	0.54
NSG123 +0.05at%Al	20	26,500	89.3	1.6	0.09
	40	21,400	90.9	1.4	0.05
	60	11,100	90.9	2.3	0.37
NSG123 +0.1at%Al	60	14,400	91.2	1.7	0.36

at 100 K for NSG123 sample increases with increasing cooling rate. This means that there is not enough time to promote the grain growth of NSG123 when the cooling rate is fast. In the case of samples doped Al, one can see that T_c values slightly decrease and ΔT_c values become wider, comparing with that of NSG123. In the case of doping level lower than 0.1 at %, T_c values of samples even by fast cooling rate, which showed around 91 K with sharp transition, were hardly influenced by Al doping.

Azzouz *et al.* reported that the T_c and the J_c value of YBCO bulks with Al_2O_3 doping level as low as 0.2 wt% indicated relative insensitivity to Al_2O_3 content [10]. However, our doping level is rather low comparing with their Al addition into YBCO. On the other hand, the effect of Al incorporation has been reported by Siegrist *et al.* [13]. They showed that the T_c dropped gradually for x value lower than 0.1, then decreased drastically with increasing Al concentration due to Al substitution only into Cu site in $Ba_2YCu_{3-x}Al_xO_7$. This tendency is in good agreement with present result.

It is favorable from the viewpoint of engineering production as high quality RE123 filaments can be inexpensively fabricated in a short time. Therefore, the microstructure and superconducting properties for samples treated at fast cooling rate of 60°C/h are hereafter discussed.

Fig. 2 shows typical SEM photographs of fractured and polished surfaces in the longitudinal cross-section of the samples. The texture of samples doped with Al shown in Figs. 2(b) and 2(c) have an aligned dense structure compared with that of Fig. 2(a). The grey $(Nd, Sm, Gd)_2BaCuO_5$ (NSG211) particles can be seen in all high-magnification photographs. It should be noted that a large number of fine NSG211 particles, with mean diameter of about 1 μm were dispersed in dark NSG123 matrix Fig. 2(b). The number of finely dispersed NSG211 particles increases and the average particle size decreases when 0.05 at% Al is doped. On the other hand, large Cu-rich phases indicated by arrow A can be observed in 0.1at% Al doped sample. An EDX analysis of this regions with dimensions approximately 2 μm × 2 μm on the cross-sectional surface represented compositional ratio of $(Nd, Sm, Gd) : Ba : Cu : Al = 11.72 : 16.5 : 71.4 : 0.37$,

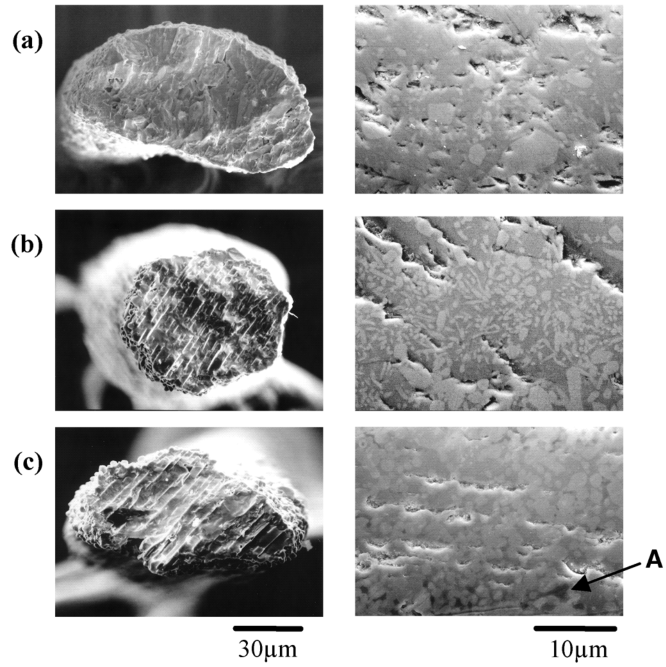

Fig. 2. SEM photographs of the fracture surface and the polished surface on the longitudinal cross-section. Samples were partially melted at 1050°C and cooled at a rate of $60^\circ\mathrm{C/h}$. (a) NSG123, (b) NSG123+0.05%at Al, and (c) NSG123+0.1 at% Al.

indicating a stoichiometric deviation from the 123 compositional ratio. In addition, Al-rich region can be observed in grain boundary between NSG123 phases. It suggests that chemically doped Al probably forms stable $\mathrm{Al_2O_3}$ and/or the Al-related compound which Al reacts Ba and Cu in liquid during partial melting. In peritectic reaction, thus formed these very small particles act as primary nucleation site for the NSG211 and then promote growth of NSG123 grains resulting in well oriented microstructure. Accordingly, the size reduction of NSG211 is presumably attributed to the increased number of nucleation site by a small amount of Al doping. Even when the cooling time from NSG211+liquid is short, the Al addition is expected to reduce the size of NSG211 due to both reduction the surface energy between small size 211 particle and liquid and the low concentration of the Al atom at the interface by a small amount of doping. From XRD analysis, it was found that the crystal structures of pure NSG123 were a mixture of a dominant NSG123 phase and NSG211. However, we could not detect any peaks corresponding to Al and its related compounds such as $\mathrm{Al_2O_3}$ in all samples with Al doping lower than 0.1 at%, because the size of Al-rich phase was presumably too small and additional Al concentration was rather low.

In the case of Zr and Sn doping, it was reported that Ba preferably formed $\mathrm{BaZrO_3}$ and $\mathrm{BaSnO_3}$ through the heat treatment and fine these particles acted as effective pinning centers in bulk RE123 samples [1]–[3], [6]–[9]. A possibility that Al reacts with Ba or Cu and fine compound particles or Al substitution into Cu site as reported [13] act as a pinning center is acceptable from the fact that the J_c value of Al-doped sample is improved.

Next, the field dependence of transport J_c for filamentary samples was examined in an applied magnetic field up to 15 T at the temperature range from 77 K to 90 K. Fig. 3 shows J_c at various temperatures as a function of applied magnetic field for the NSG123 samples. Because the samples were sometimes burnt out by applying the current larger than 0.5 A, critical current I_c value was limited to 0.3 A in the $J_c - B$ measurement. In the case of pure NSG123 cooled at a rate of $60^\circ\mathrm{C/h}$, the J_c value at 77 K decreases by applying a magnetic field of 0.1 T, indicating weak-link behavior at the grain boundaries. Although weak-link behavior is assumed to originate from a dirty grain boundary due to impurities and cracks, indeed, $60^\circ\mathrm{C/h}$ cooled NSG123 shows relative high resistivity as shown in Table I. The J_c value gradually decreases with continuously increasing the applied magnetic field, and the superconductivity disappears at around 10 T. On the other hand, while the J_c value of both Al doped samples decrease with increasing the applied magnetic field, a J_c value of higher than $10^3\ \mathrm{A/cm^2}$ is maintained up to around 10 T. It is found that Al doping was effective in increasing both the J_c value and the irreversibility field.

From the difference in $J_c - B$ behavior, in order to study what kinds of flux pinning centers act, we investigated flux pinning mechanism based on an analysis of the normalized volume pinning force at the reduced field. Normalized volume pinning force density, $F_p/F_{p,\max}(F_p = J_c \times H_a)$ as a function of reduced field, $h = H_a/H_{irr}$ is also shown in lower row of Fig. 3. The data of H_{irr} was obtained from $J_c - B$ curve using the criterion of $10\ \mathrm{A/cm^2}$. The following consideration is obtained: 1) Peak positions for pure NSG123 sample located at around h = 0.3–0.4 which was close to $h = 0.33$, suggesting that normal and point pinning are dominant [14]. As seen in SEM observation, NSG211 particles were dispersed after melting. 2) The case of 0.05 at% Al sample, the peak position of 77 K locates at around $h = 0.43$, which is close to the position of theoretically predicted for $\Delta\kappa$ pinning due to compositional fluctuations of $\mathrm{(Nd,Sm,Gd)_{1+x}Ba_{2-x}Cu_3O_y}$ solid solution (NSG123ss) clusters with small x value. 3) Peak position $h = 0.4$, which is medium position of $\Delta\kappa$ pinning and normal and point pinning, of 83 K for 0.1at% Al added sample gradually shifts to lower reduced fields with increasing temperature. In a high temperature region near T_c, the effect of flux creep should be considered and the superconductivity may be unstable due to thermal activation energy. Furthermore, NSG123ss clusters with lower T_c value may exist as normal particles at higher temperatures. Therefore, we consider that pinning contribution for Al doped sample was owing to overlapping the field induced pinning, NSG123ss clusters, and homogeneous distribution of NSG211 particles and nano-scale particles of $\mathrm{Al_2O_3}$ and Al related compounds.

IV. Conclusion

The effect of Al doping on transport critical current density and microstructure of filamentary NSG123 superconductor processed via chemical route was investigated. Maximum J_c value of $3.0 \times 10^4\ \mathrm{A/cm^2}$ at 77 K and 0 T was obtained for the pure NSG123 sample partially melted at 1050 °C and cooled at a rate of $40^\circ\mathrm{C/h}$. However, the J_c value of a sample cooled by fast rate was drastically decreased and it was $3.1 \times 10^3\ \mathrm{A/cm^2}$ at most. Even fast cooling rate of 60 °C/h, the 0.05at%Al-doped sample and the 0.1at%Al-doped sample showed the J_c values of $1.1 \times 10^4\ \mathrm{A/cm^2}$ and $1.4 \times 10^4\ \mathrm{A/cm^2}$. The Al-doped samples

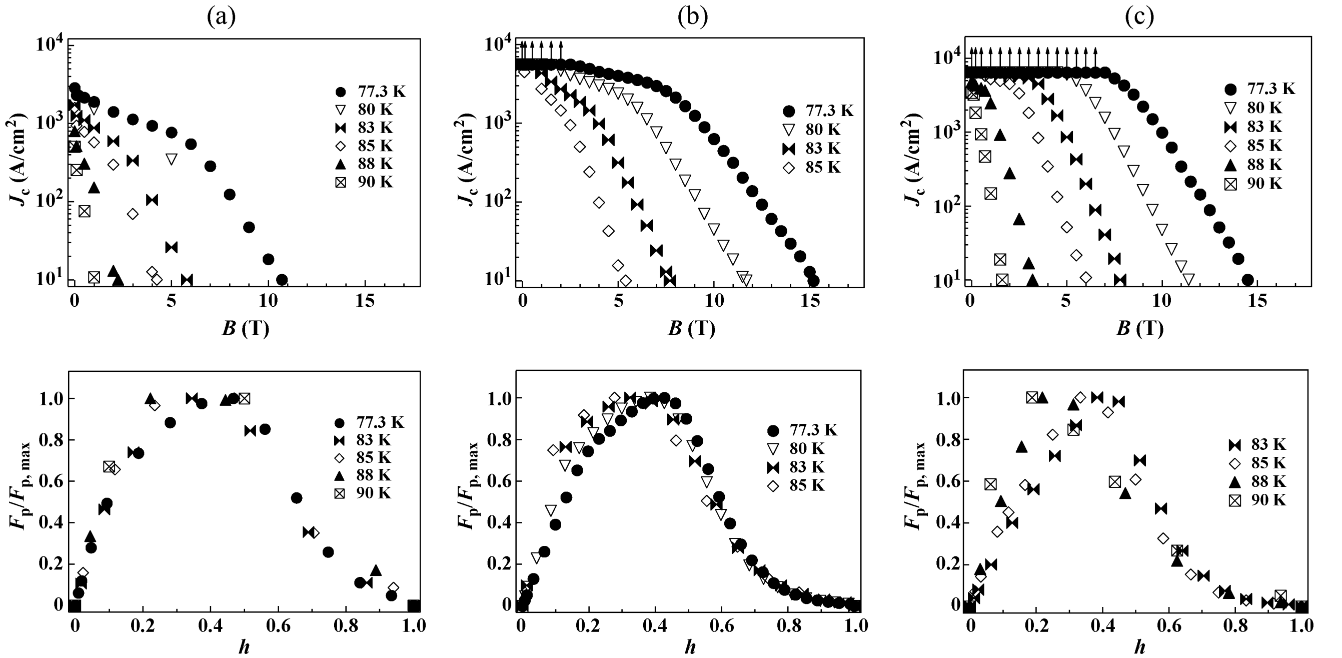

Fig. 3. Field dependence of J_c and volume pinning force as a function of reduced field. Samples were partially melted at 1050°C and cooled at a rate of 60°C/h. (a) NSG123, (b) NSG123+0.05 at% Al, and (c) NSG123+0.1 at% Al.

exhibited a layered dense microstructure, in which fine NSG211 particles were homogeneously dispersed. From J_c measurement in applied magnetic field, the J_c value of Al free sample gradually decreased with increasing applied magnetic field and the superconductivity was disappeared around 10 T. In contrast, a J_c value higher than 10^3 A/cm^2 was maintained up to 10 T for both 0.05at% Al and 0.1 at% Al doped samples. In conclusion, Al chemical doping to NSG123 was found to be effective in homogeneous dispersion of NSG211 and the reduction of the size of NSG211 particles. In addition, a small amount of Al doping is also a significant factor for enhancement of both the J_c in a magnetic field and the irreversibility field.

ACKNOWLEDGMENT

This work was performed at the High Field Laboratory for superconducting Materials, Institute for Materials Research, Tohoku University.

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