Influence of Precursor Composition on the Microstructure and Superconducting Properties of Dy-Ba-Cu-O filaments

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Abstract. Dy-Ba-Cu-O filaments have been successfully fabricated by a solution spinning method. The relationship between the partial melting temperature and the transport $J_c$ value at 77 K of the filamentary sample was systematically investigated. Two kinds of precursor filaments with starting composition of Dy:Ba:Cu = 1.18:2.12:3.09 (sample A) and Dy:Ba:Cu = 1.00:2.00:3.00 (sample B) were partially melted in 1%O2+Ar atmospheric gas and oxygenated in pure 100% O2 gas. Samples partially melted at a wide temperature range of 990-1040 °C had $J_c$ values higher than $10^4$ A/cm². Both sample A and sample B partially melted at 1020 °C exhibited the maximum $J_c$ value higher than $4.2 \times 10^4$ A/cm² and $2.0 \times 10^4$ A/cm², respectively. These samples had a dense microstructure consisting predominantly of Dy123 and finely dispersed Dy211 particles. The Dy211 particles with a diameter of about 1 μm were finely dispersed in sample A, while the particles with a diameter of about 5 μm were observed in sample B. The $J_c$ values of both samples were maintained about $2.0 \times 10^3$ A/cm² up to 14 T.

1. Introduction

By melt-texture processing for REBa$_2$Cu$_3$O$_y$ (RE123; RE: rare earth) superconductors, critical current density ($J_c$) values at 77 K have improved to a practical level even in high magnetic fields. Further $J_c$ enhancement to the level of $10^5$ A/cm² and a reduced degradation in high magnetic fields at 77 K are required for better performance. In order to achieve high $J_c$ value, the introduction of effective pinning centres is essential. It is known that RE$_2$BaCuO$_5$ (RE211) dispersed in the RE123 superconductor acts as a strong pinning centre. Recently, Nariki et al reported that the $J_c$ value of the Dy123 bulk superconductor was significantly enhanced by refining RE211 inclusions [1, 2]. Through systematic examination, they showed that several conditions such as Dy211 particle size, the amount of Dy211 addition and oxygen annealing temperature influenced the superconducting properties of Dy123 superconductors and $J_c$ behaviour [1, 2]. In addition, bulk Dy-Ba-Cu-O (Dy123) superconductors with fine Dy211 additions showed superior trapping of high magnetic fields at 77 K, which exceeded the capacity of melt-textured Y123 bulk superconductors [3, 4].

From the viewpoint of practical applications for superconducting magnets and power transmission cables operated at 77 K, it is important to establish a fabrication technique for high quality fine filaments of superconducting materials. Various processing techniques to fabricate the super-
conducting wire has been developed to realize high $J_c$. Although the powder-in-tube (PIT) process is popular among these techniques, it is unfortunately required to overcome an expensive fabrication cost, many difficult steps to form fine wire and selection suitable sheath materials. A solution spinning method is a relatively simple and low cost technique which easily permits long and fine wire fabrication [5]. However, few studies have been carried out towards establishment of the preparation techniques and the improvement of superconducting properties for wire type Dy123 compared with the bulk Dy123 superconductors.

In this paper, the preparation and characterization of filamentary Dy123 superconductors with different starting composition fabricated by a solution spinning method and the effect of starting composition on $J_c$ are examined. The field dependence of transport $J_c$ at 77 K for the optimally fabricated filamentary Dy123 superconductors is also investigated.

2. Experimental

The experimental procedure was almost the same as used in the previous study [6]. A brief description is given here. Two kinds of precursor filaments with starting composition of Dy:Ba:Cu = 1.18:2.12:3.09 (sample A) and Dy:Ba:Cu = 1.00:2.00:3.00 (sample B) were fabricated by a solution spinning method through a homogeneous aqueous solution containing acetates of Dy, Ba and Cu, poly(vinyl alcohol), propionic acid and 2-hydroxy isobutyric acid. After concentrating the solution in order to obtain a stable viscous homogeneous spinning precursor, the precursor was extruded through a stainless nozzle as a filament into a hot air zone, and coiled on a winding drum. After calcination, the precursor filament was partially melted in flowing 1%O2+Ar gas at various temperatures and then oxygenated by a two-step treatment in flowing pure O2 gas.

The $T_c$ and the transport $J_c$ at 77 K were measured by a standard DC four-probe resistive method. The sample was embedded on the substrate at an arbitrary direction for the sample diameter using epoxy resin and mounted on a critical-current-measuring holder. External magnetic fields were applied in a direction perpendicular to the filament length using a helium-free 15 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 microstructure of the sample was also studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX).

3. Experimental results and discussion

The diameter of both filament samples after partial-melting was about 50 - 90 μm. All samples partially melted in a temperature range of 980 - 1080 °C showed metallic behaviour from room temperature to $T_c$ (onset), and attained zero resistivity at 86 - 90K. Since the $J_c$ value was sensitive to the partial melting temperature, we first studied the effects of varying temperature during partial melting on the superconductivity. Figure 1 shows the relation between the partial melting temperature and transport $J_c$ at 77 K and self- field of filamentary samples. To protect the sample from burning out, the applied current was less than 1.0 A. Therefore, the arrow in figure represents the value when a current of 1.0 A was applied. It is found that the $J_c$ values of both samples dependent on partial melting temperature and $J_c$ value higher than 10^4 A/cm² are obtained over a wide temperature range of 980 - 1040 °C. The samples partially melted at around 1020 °C shows maximum $J_c$ value of higher than 4.2x10^4 A/cm² for sample A and 2.0x10^4 A/cm² for sample B, respectively. For the filamentary Dy123 superconductor, the optimum melting temperature in flowing 1%O2+Ar was higher by 40 °C than the peritectic decomposition temperature in 1%O2+Ar [7]. Although the $J_c$ value of sample B is low compared with that of sample A, the reproducibility of $J_c$ value for sample B was superior to sample A.

Next, we studied the crystal structure of the samples partially melted at 1020 °C. Figure 2 represents the XRD patterns of the samples partially melted at 1020 °C, which shows the highest $J_c$ in each series. The peaks corresponding to Dy123 and the impurity Dy,BaCuO (Dy211) are observed. Although, some RE211 particles are always found in the melted processed microstructure due to an
incomplete peritectic reaction, it should be noted that an amount of Dy211 phase in the present samples melted in 1%O2+Ar was extremely high as compared with filamentary Eu123 and Sm123 samples melted in the same manner [6,8]. This characteristic feature, that is the formation of 211 phase particularly increases during melt processing in low oxygen partial pressure, may be particular to the present filamentary Dy123 superconductors.

Figure 3 shows typical SEM photographs of the polished and etched surfaces on the longitudinal cross-sections of the samples shown in figure 2. Both samples have a relatively dense structure. A number of Dy211 particles with diameter less than 1 μm were observed in sample A, while Dy211 particles with diameter about 5 μm were dispersed in sample B which are indicated the arrow A and arrow B in photographs. Nevertheless sample B starts from the chemical-liquid phase with compositional ratio of Dy:Ba:Cu=1:2:3, it was observed that sample B indicated stoichiometric deviation from the stoichiometric composition of Dy:Ba:Cu=1:2:3 to a Dy-rich compositional ratio from EDX analysis on the longitudinal cross-sectional whole surface. Nariki et al reported that bulk Dy123 mixed with 40 mol % Dy211 showed the highest $J_c$ at 77 K and 0 T compared with those of the samples with lower than 40 mol % Dy211 [1]. They have succeeded in dispersing Dy211 particles of size less than 0.6 μm in bulk Dy123, which leads to an enhancement in $J_c$ to over $7 \times 10^4$ A/cm$^2$ at 77 K and self-field.

The field dependence of $J_c$ for samples was examined in an applied magnetic field up to 14 T at 77 K. Figure 4 shows $J_c$ value at 77 K as a function of applied magnetic field for the filamentary samples. The samples are the same as these presented in figure 2. The $J_c$ value for both samples drastically decreases to less than $1.0 \times 10^4$ A/cm$^2$ by applying only a magnetic field of 1 T due to the weak-link behaviour at the grain boundaries. Both samples show a plateau in the $J_c$-$B$ curves at 3-around 11 T and serious deterioration of $J_c$. $J_c$ values of both samples are maintained about $2.0 \times 10^3$ A/cm$^2$ up to 14 T. Inoue et al have investigated the effect of Dy211 particle size on the pinning properties of Dy123/Dy211 composites and showed that the $J_c$ value was enhanced by reducing the Dy211 particle size to about 0.63 μm in average diameter, particularly in a low and high field region [2]. While our transport $J_c$ value is not so high as compared with their data measured by DC magnetization, our results of $J_c$ behaviour agree qualitatively with theirs in a magnetic field. It is found that homogenous dispersion of fine Dy211 particles is effective for the improvement in $J_c$ of filamentary samples.
4. Conclusions
Dy-Ba-Cu-O filaments with different starting composition were fabricated by a solution spinning method. Two kinds of precursor filaments with starting composition of Dy:Ba:Cu = 1.18:2.12:3.09 (sample A) and Dy:Ba:Cu = 1.00:2.00:3.00 (sample B) were partially melted in 1%O₂+Ar atmospheric gas and oxygenated in pure 100% O₂ gas. It was found that the superconducting properties of Dy123 filaments were strongly dependent on the heating condition. Samples partially melted at a wide temperature range of 990 - 1040 °C represented $J_c$ value higher than $10^4$ A/cm². Both sample A and sample B partially melted at 1020 °C for 30 minutes exhibited the $J_c$ value higher than $4.2 \times 10^4$ A/cm² and $2.0 \times 10^4$ A/cm², respectively. These samples had a dense microstructure consisting dominant Dy123 phase and finely dispersed Dy211 particles. The Dy211 particles with diameter of less than 1 μm were finely dispersed in sample A, while the particles with diameter of about 5 μm were observed in sample B. Although the $J_c$ value for both samples drastically decreases to less than $1.0 \times 10^4$ A/cm² by applying only a magnetic field of 1 T, the $J_c$ values of both samples were maintained about $2.0 \times 10^3$ A/cm² up to 14 T.

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References
[1] Nariki S, Murakami M 2002 Supercond. Sci. Technol.15 786.
[2] Inoue K, Nariki S, Murakami M 2001 Physica C 378-381 755.
[3] Latha B, Ikuta H, Mizutani U 2004 Jpn. J. Appl. Phys. 43 970.
[4] Nariki S, Sakai M, Murakami M 2004 Physica C 412-414 566.
[5] Goto T, Sugishita T 1991 Jpn. J. Appl. Phys. 30 L997.
[6] Ban E, Goto T, Watanabe K, Matsuoka Y 2002 Jpn. J. Appl. Phys. 41 L1055.
[7] Murakami M Handbook of Superconducting Materials, ed. Cardwell D A 2003 IOP 331.
[8] Ban E, Goto T, Matsuoka Y 2003 Physica C 388-389 411.