Effect of Zr and Zn Doping on Critical Current Density of Filamentary Dy-Ba-Cu-O Superconductors

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Abstract. The effect of Zr and Zn doping on transport critical current density and microstructure of filamentary Dy-Ba-Cu-O superconductor was investigated. Precursor filaments prepared by a solution spinning method were partially melted in atmosphere gas and oxygenated. Samples doped with Zr and Zn showed dense microstructure, and finely dispersed Dy2BaCuO5 particles in the Dy123 matrix were observed. It was found that the superconducting properties of Dy123 filaments doped with Zr and Zn were strongly dependent on the heating condition and the atmosphere. A high $J_c$ value more than $10^4$ A/cm$^2$ with good reproducibility was obtained when these samples partially melted in flowing 20% O$_2$+Ar gas. By controlling the heat treatment condition, the maximum $J_c$ value of $2.7 \times 10^4$ A/cm$^2$ at 77 K and self-field were attained for the sample doped with 0.1 at% Zr. In the case of the sample doped with 0.1 at% Zn, the $J_c$ value around $2.5 \times 10^4$ A/cm$^2$ was obtained, which was comparable with that of sample without doping. The relation between the field dependence of $J_c$ and microstructure of the filamentary sample was also examined.

1. Introduction

Melt-processed REBa$_2$Cu$_3$O$_7$ (RE123; RE: rare earth) bulk superconductors exhibit good pinning performance at high magnetic fields. They are expected for applications such as superconducting magnets with high trapped field, flywheels for energy storage, current lead materials, etc. DyBa$_2$Cu$_3$O$_7$ bulk superconductors have attracted due to high critical current density ($J_c$), peak effect in the $J_c$-B curves and preferable trapped magnetic flux density exceeding to those of the melt-textured YBa$_2$Cu$_3$O$_7$ bulk superconductors[1,2].

In order to achieve high $J_c$ value, the introduction of effective pinning centres is essential. It is known that doping by different metal elements can change the microstructure of grain boundary and cause the formation of fine precipitation in the RE123 matrix, which contribute significantly to the value of $J_c$. Recently, Latha et al have succeeded in the enhancement of both $J_c$ and trapped flux density at 77 K in ZnO doped Dy123 bulk superconductors [3]. Furthermore, Orlova et al have reported that the addition of 1-5 wt% of ZrO$_2$ into Dy123 leads to formation of clean boundaries and enhancement of flux pinning in a magnetic field [4]. However, the superconducting properties of the chemically doped Dy123 have not yet been widely investigated. Few investigations have been
particularly carried out towards the effect of metal elements doping on superconducting properties of filamentary Dy123 superconductor.

In this paper, we have studied the effect of Zr and Zn doping on the microstructure and transport $J_c$ in the filamentary Dy123 superconductors.

2. Experimental

A filamentary Dy123 superconductors with and without doping were fabricated by a solution spinning method. The precursor with the nominal composition of Dy:Ba:Cu =1:2:3 was synthesized from a homogeneous aqueous solution containing acetates of Dy, Ba and Cu, poly(vinyl alcohol), propionic acid and 2-hydroxy isobutyric acid. Either Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O or ZrCl$_2$ $\cdot$ 8H$_2$O was also added into an aqueous solution, to produce sample of Dy123 with Zn or Zr in atomic ratio of 0.1%, and thoroughly mixed. After concentration of the solution in order to obtain a stable viscous homogeneous spinning dope, the dope was extruded through the stainless nozzle as a filament into a hot air zone, and coiled on a winding drum. The precursor filament with 150-200 μm in diameter was calcined at 900°C for 15min in flowing oxygen to remove volatile components and CO$_2$ completely. Samples were partially melted under various heating conditions in flowing atmosphere gas, and then cooled in two steps. After partial-melting, samples were oxygenated by a two-step treatment in flowing pure O$_2$ gas.

The $T_c$ and transport $J_c$ at 77 K were measured by a standard DC four-probe resistive method. 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 the filament samples after partial-melting was about 60-90 μm. Optimum atmosphere gas condition during partial melting to obtain high $J_c$ at 77 K and self-field was first investigated. The partial melting process was carried out using some kinds of argon base gases with various oxygen concentrations and pure oxygen gas. It was found that the $J_c$ values at 77 K and 0 T significantly depended on the oxygen concentration in an atmosphere gas. Sample partially melted in flowing 20%O$_2$+Ar showed high $J_c$ value at 77 K and self-field, and good reproducibility of $J_c$ compared to those of samples partially melted in 100% oxygen, 3%O$_2$+Ar and 1%O$_2$+Ar. Therefore, we discussed hereafter the filamentary samples partially melted in 20%O$_2$+Ar atmosphere gas.

Figure 1 shows transport $J_c$ at 77K and self-field as a function of the partial melting temperature. In
the case of Dy123 doped with Zr, high $J_c$ value higher than $10^4$ A/cm$^2$ is obtained over a wide temperature range of 1030 - 1080 °C. The sample partially melted at 1070°C shows the highest $J_c$ value of $2.7 \times 10^4$ A/cm$^2$. On the other hand, the $J_c$ value of $2.5 \times 10^4$ A/cm$^2$ is obtained for Dy123 doped with Zn melted at 1050 °C, which was comparable with that of doping free sample. In the case of Zn doping, temperature region in which can be obtained high $J_c$ is relatively narrow.

The undoped sample exhibits normal-state resistivity ($\rho$) of 0.11 mΩ cm at 150 K and $T_c$ value of 91.6 K with a sharp transition of 1.5 K in width, which indicates that a single high $T_c$ phase is formed. The $\rho$ values at 150K and $T_c$ values of sample doped with Zn partially melted at 1050°C and samples doped with Zr partially melted at 1070°C were 0.18 mΩ cm and 90.1 K and 0.26 mΩ cm and 89.5 K, respectively. Both samples with Zn or Zr exhibit the lower $T_c$ value with a slightly broad transition of about 1.7 K compared with that of the sample without doping. Although the value of $T_c$ slightly suppressed by Zn or Zr doping, serious depression in $T_c$ for the present samples was not observed due to the low doping level.

The crystal structure of three kinds of samples was a mixture of a dominant Dy123 phase and secondary Dy$_2$BaCuO$_5$ (Dy211) phase. The distinct reflection peaks corresponding to Dy211 were noticeable in XRD patterns of all filaments, and the reflections corresponding to Zr or Zn and metal element related compounds could not be detected. Figure 2 shows typical SEM photograph of the fracture surface of the Zr doped sample and high-magnification SEM photographs of the polished and etched surface on the longitudinal cross-section of three kinds of samples. Scale bars represent 10μm. One can see in fracture surface that the texture of sample has a relatively dense structure. The grey particles are the Dy211 particles as can be seen in high-magnification photographs. A number of fine Dy211 particles with diameter less than 1 μm were dispersed in the sample with doping. The number of dispersed Dy211 particles increased and the average particle size decreased when Zn or Zr is doped. An EDX analysis on the longitudinal cross-sectional surface region with dimensions approximately 30 μm × 30 μm shown in lower row of figure 2(c) and 2(d) represented the compositional atomic ratio of Dy:Ba:Cu=1.59:2.00:3.08 and Dy:Ba:Cu=1.80:2.00:3.31, which indicated serious stoichiometric deviation from the 123 to Dy-rich compositional ratio after melt process. It is known that the amount of oxygen defects is reduced by the refinement of Dy211 particles, since the Dy211/Dy123 interfaces promote oxygen diffusion. Nariki et al have succeeded in dispersing Dy211 particles of size of less than 0.6 μm in the bulk Dy123, which leads to an enhancement in $J_c$ to over $7 \times 10^4$ A/cm$^2$ at 77 K and self-filed [5]. Finely and homogenous dispersion of Dy211 particles is effective for the improvement of $J_c$ for filamentary samples with dense structure, which is the same tendency as bulk superconductor.

Figure 2. SEM photographs for the fracture surface (a) and polished and etched surface on the longitudinal cross-section (b)-(d). (a) and (d) Dy123 +0.1 at% Zr, (b) Dy123 without doping and (c) Dy123 +0.1 at% Zn.

Figure 3. Field dependence of the critical current density at 77 K for three filamentary Dy123 samples.
The field dependence of $J_c$ for filamentary samples was examined in an applied magnetic field up to 14 T at 77 K. Figure 3 shows $J_c$ value at 77 K as a function of applied magnetic field for the filamentary samples. The samples are the same as those presented in figure 2. The $J_c$ value for all 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 behaviours at the grain boundaries. In the case of samples doped with Zn and Zr, deterioration of $J_c$ values in magnetic field is noticeable. The $J_c$ value for both samples with doping decreases with increasing the applied magnetic field and the superconductivity disappears by applying a magnetic field of around 11 - 12 T. On the contrary, the $J_c$ value for sample without doping decreases with increasing the applied magnetic field, $J_c$ value around $2.8 \times 10^4$ A/cm$^2$ is maintained by applying the field up to 14 T. However, we could not observe a peak effect in present samples, while a pronounced peak effect in magnetization $J_c$-$B$ curve was observed for bulk-type Dy123 [1,3]. The addition of Zn and Zr into filamentary Dy123 results in the poor $J_c$-$B$ behaviour. As seen in SEM observation, the microstructure of Zr or Zn added Dy123 after melting is inhomogeneous.

Iida et al have reported that a small amount of ZrO$_2$ addition causes significant particle pushing phenomena due to increased interfacial energy and results in homogeneous microstructure [6]. Latha et al have reported the effect of Zn doping for melt processed Dy123 bulk that Zn$^{2+}$ ions locally breaks the superconducting pairs producing a spatial distribution of weak superconducting region [3]. In the case of Zr doping in melt processed Dy123, it was shown that fine Dy211, BaZrO$_3$, particles reacted with Ba element acted as pinning centres [4]. These possibilities can not be denied absolutely for our filamentary samples either. The $J_c$ was enhanced by Zr doping in a zero magnetic field due to refinement of Dy211 particles. Although the detailed mechanism is not clear at the present stage, an inferior field dependence of $J_c$ may be due to the inhomogeneous microstructure. By changing both the doping element and concentration into Dy123, details on the Zn and Zr doping are under investigation.

4. Conclusions
The effect of Zr and Zn doping on transport critical current density and microstructure of filamentary Dy123 superconductor prepared by a solution spinning method was investigated in comparison with the undoped Dy123 sample. A high $J_c$ value more than $10^4$ A/cm$^2$ with good reproducibility was obtained for the sample partially melted in flowing 20%O$_2$+Ar gas. By controlling the condition, the maximum $J_c$ value of $2.7 \times 10^4$ A/cm$^2$ at 77 K and self-field was attained for the sample doped with 0.1 at% Zr. In the case of the sample with 0.1 at% Zn, the $J_c$ value around $2.5 \times 10^4$ A/cm$^2$ was obtained, which was comparable with that of sample without doping. Both doped samples had dense microstructure and a number of fine Dy211 particles with diameter less than 1 μm were dispersed in the Dy123 matrix. The superconductivity of samples doped with Zn and Zr disappeared by applying a magnetic field of around 11-12 T. Zn and Zr doping into filamentary Dy123 resulted in the poor $J_c$-$B$ behaviour.

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