Transport Critical Current of Filamentary Zr-Doped Gd-Ba-Cu-O Superconductors in High Magnetic Fields

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Transport Critical Current of Filamentary Zr-Doped Gd-Ba-Cu-O Superconductors in High Magnetic Fields

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***Abstract*—Filamentary Gd-Ba-Cu-O superconductors doped with nominal Zr concentrations between 0 and 0.5 at% relative to Gd123 were prepared by a solution spinning method. Samples were partially melted in flowing 20% O_2 + Ar atmosphere gas at various partial melting temperatures and oxygenated in pure oxygen gas. High J_c value of 2×10^4 A/cm^2 at 77 K and 0 T were obtained for the Gd123 + 0.1at%Zr sample optimally processed. In the case of doping levels less than 0.5 at %, T_c values, which were about 92 K with sharp transitions, were hardly influenced by Zr concentration. From transport critical current measurements in magnetic fields, the J_c value of the pure Gd123 filament sharply decreased with increasing applied field. Gd123 with 0.5 at%Zr doping processed under optimum conditions showed little deterioration of J_c values in low magnetic fields and J_c values higher than 10^3 A/cm^2 was maintained up to 14 T. It was also found that J_cs in high magnetic field and the irreversibility field were improved by a small amount of Zr doping.**

***Index Terms*—Critical current density, Gd-Ba-Cu-O filament, magnetic field behavior, Zr chemical doping.**

I. Introduction

MELT-PROCESSED LRE-Ba-Cu-O (LRE123, LRE = light rare earth) superconductors are promising candidates for various practical applications such as superconducting magnets with high trapped field, flywheels for energy storage and current lead materials. Encouraging for the use of LRE123 materials for practical applications, critical current density (J_c) values at 77 K have improved to a practical level even in high magnetic fields by many developments of melt-textured processing. Further J_c enhancement to the higher level of 10^5 A/cm^2 and a reduced degradation in high magnetic fields at 77 K are required 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 oxide particles is one of the most useful techniques to enhance the J_c and the magnetic flux pinning. However, technical difficulties arise in the area of the artificial defect introduction into LRE123 matrix, due to a balance between the enhancement of pinning strength and the degradation of the superconductivity.

Studies of the LRE123 system with additional impurities have gained considerable attention and excellent electromagnetic performance. Among them, (Nd,Eu,Gd)123 bulks with contaminated Zr particles showed both a J_c value of around 2×10^5 A/cm^2 at 77 K and an enhanced pinning at liquid oxygen temperatures [1]. Furthermore, an enhancement of both the J_c of about 10^5 A/cm^2 at 77 K and the trapped flux density at 77 K in ZrO_2 doped Gd123 bulk superconductors were demonstrated [2]. Other researchers demonstrated the potential of Zr and/or its compound to play an important role in effective pinning [3], [4]. However, the effect of doping on the superconducting properties of fine filament type LRE123 superconductors has not yet been widely investigated except for a few experiments [5]. Therefore, further studies for wire or filament type superconductors with additional impurities prepared by a low cost process are needed to establish the fundamental data and to enhance the superconducting properties.

In this study, we deal with fine Gd123 filaments prepared by a low cost and fast fabrication process via a chemical route, and our purpose is to investigate the influence of Zr chemical doping on microstructures and transport J_c behavior in a magnetic field ranging from 0 to 17 T for the filamentary Gd123 superconductors.

II. Experimental Procedure

Filamentary superconducting samples were fabricated by a solution spinning method as described elsewhere [6]. The precursor Gd123 filament with the starting composition of Gd : Ba : Cu = 1.18 : 2.12 : 3.09 was synthesized from a homogeneous aqueous solution containing metal acetates of Gd, Ba and Cu, poly(vinyl alcohol), propionic acid and 2-hydroxy isobutyric acid. Various amounts of Zr ranging from 0.1 to 0.5 at% using zirconium dichloride oxide octahydrate, $ZrCl_2O \cdot 8H_2O$ 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 Cl_2 and CO_2. Samples were partially melted at temperatures between 1040 °C and 1090 °C for 30 min partially melted in flowing 20% O_2+Ar gas, and then the samples were cooled in two steps, first cooling step from partial-melting temperature to 900 °C was at a rate of 30°C/h

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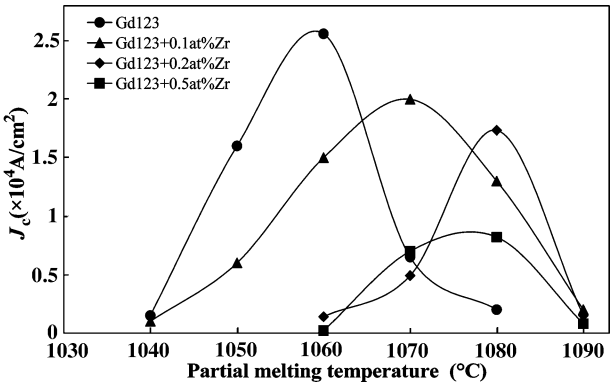

Fig. 1. Transport Jc at 77K and self-field as a function of partial-melting temperature for filamentary Gd123 samples with Zr doping concentrations 0–0.5 at%.

and second step from 900 °C to 500 °C was at a rate of 50°C/h. The oxygenation was finally carried out by a two-step treatment, 500 °C/5 h + 340°C/10 h, in flowing pure O_2 gas.

The T_c and transport J_c were measured by a standard DC four-probe resistive method. 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 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

The diameter of filamentary samples after partial melting was about 80–100 μm. Fig. 1 shows transport J_c at 77 K and self-field as a function of the partial melting temperature in flowing $20\%O_2 + Ar$ gas. It can be seen from this figure that high J_c values larger than 10^4 A/cm^2 is obtained in the samples doped with low Zr content less than 0.2 at% and pure Gd123. Although Zr 0.1at% sample shows J_c value higher than 10^4 A/cm^2 over a wide temperature range of 1060–1080 °C, 0.5 at% Zr doped sample exhibits low J_c value of 8.2×10^3 A/cm^2 at most. When Zr is added into Gd123, the optimum melting condition obtained high J_c value shifts to higher temperature region. A similar tendency for optimum melting condition was observed in our filamentary Zr doped Sm123 superconductors.

Table I summarizes the transport J_c value at 77 K and self-field, T_c, transition width ΔT_c, and resistivity at 100 K of three kinds of Gd123 samples processed at optimum partial melting temperature. Significant difference in J_c between samples can

TABLE I
Superconducting and Electrical Properties of Filamentary Samples Melted at Optimum Temperature

sample	optimum T_s(°C)	J_c (A/cm^2)	T_c (K)	ΔT_c (K)	ρ (mΩ·cm)
Gd123	1060	25600	91.9	1.78	0.06
Gd123 +0.1at%Zr	1070	20000	91.9	2.06	0.05
Gd123 +0.5at%Zr	1080	8200	92.1	2.06	0.19

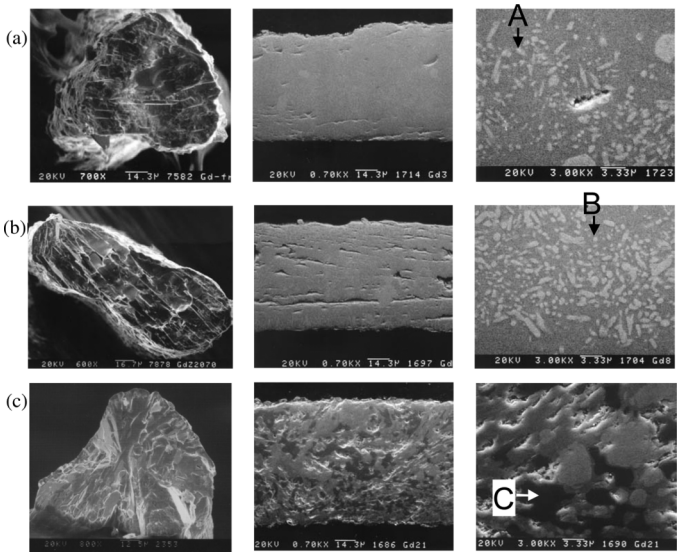

Fig. 2. SEM photographs of the fracture surface and the polished surface on the longitudinal cross-section. Samples were partially melted at optimum temperature in $20\%O_2$ + Ar: (a) pure Gd123, (b) Gd123 + 0.1 at% Zr and (c) Gd123 + 0.5 at% Zr.

be seen and J_c value decreases with increasing Zr content. Resistivity at 100 K for 0.5 at %Zr sample is rather high, whereas 0.1%Zr sample shows low resistivity, whose value is comparable to that of pure Gd123. There is no distinct diference in T_c and ΔT_c value between samples. In the case of low doping level less than 0.5 at %, T_c values of samples, which showed around 92 K with sharp transition, were hardly influenced by Zr concentration. Iida *et al.* reported that the T_c value of YBCO bulks with ZrO_2 doping level as low as 0.25 wt% indicated relative insensitivity of T_c to ZrO_2 content [3]. Other report concluded that ZrO_2 content below 0.5 wt% into (Nd,Eu,Gd)123 bulks were acceptable in the point of deterioration on superconducting transition [7].

Fig. 2 shows typical SEM photographs of the fractured and the polished surface in the longitudinal cross section of the samples. Samples exhibited maximum J_c value as shown in Table I are Gd123 (a) pure sample partially melted at 1060 °C, (b) 0.1at% Zr doped sample at 1070 °C and (c) 0.5at%Zr doped sample at 1080 °C, respectively. The texture of pure Gd123 shown in Fig. 2(a) has a relatively dense structure with small pores compared with those of Fig. 2(b) and (c). The gray particles indicated arrow A and B are Gd_2BaCuO_5 (Gd211) particles as can be seen in high-magnification photographs. It should be noted that a large number of small Gd211 particles with mean diameter of about 0.5–1 μm were dispersed in dark

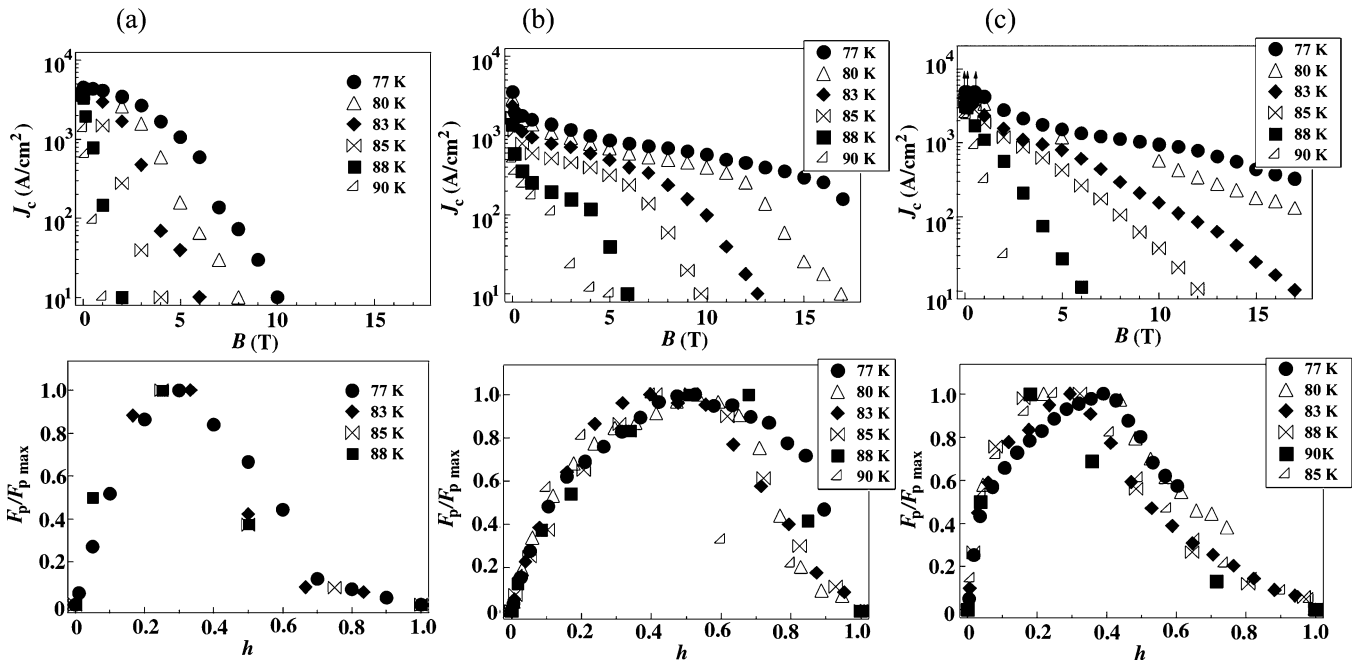

Fig. 3. Field dependence of J_c and volume pinning force as a function of reduced field: (a) pure Gd123, (b) Gd123 + 0.1 at% Zr and (c) Gd123 + 0.5 at% Zr.

Gd123 matrix as seen in Fig. 2(b) compared with that of pure Gd123 sample with large Gd211 particles of around 1–3 μm in size in Fig. 2(a). It is evident that the number of Gd211 particles increases and the average particle size becomes smaller when additional Zr is around 0.1 at%. On the other hand, large CuO phases indicated by arrow C in figure can be observed in 0.5at%Zr doped sample. An average EDX analysis data of three regions with dimensions approximately $100\,\mu\text{m} \times 100\,\mu\text{m}$ on the cross-sectional surface of 0.5at%Zr sample represented compositional ratio of Gd : Ba : Cu $= 1.73 : 2.16 : 3.00$, indicating a stoichiometric deviation from the 123 compositional ratio.

From XRD analysis for samples which were shown in Fig. 2, it was found that the crystal structures of pure Gd123 were a mixture of a dominant Gd123 phase and Gd211. While weak reflection peaks corresponding to Ba_2CuO_3 were noticeable in 0.5 at% Zr filaments, the peaks corresponding to Zr and its related compounds such as $BaZrO_3$ could not be detected in all samples. From our experimental results, we confirmed that Gd123 easily reacted with Zr and formed $BaZrO_3$ during heat treatment at about 900 °C when 5 wt% of ZrO_2 powder was added to Gd123, although the sample exhibited poor superconductivity. It was reported that Ba was preferably formed $BaZrO_3$ in the bulk RE123 sample added ZrO_2 and fine $BaZrO_3$ particles acted as pinning centers [8], [9]. However, we could not detect any trace of $BaZrO_3$ particles in these Gd123 filaments chemically doped with lower than 0.5 at% Zr by EDX analysis and/or XRD, because the particle size was probably too small and additional Zr concentration might be rather low.

Next, the field dependence of transport J_c for filamentary samples was examined in an applied magnetic field up to 17 T at the temperature range of from 77 K to 90 K. Fig. 3 shows J_c at various temperatures as a function of applied magnetic field for the Gd123 samples. Because the samples were sometimes burnt out by applying the current larger than 0.5 A, critical current I_c value was stopped at the limit of 0.3 A in $J_c - B$ measurement, therefore, J_c values at 77 K and 0 T are different from the data of Fig. 1 and Table I. In the case of pure Gd123 processed in optimum condition, the J_c value at 77 K gradually decreases with continuously increasing the applied magnetic field, and the superconductivity disappear at around 10 T. On the other hand, the J_c of 0.1 at% Zr doped sample drastically decreases by applying a magnetic field of 0.5 T, indicating weak-link behavior at the grain boundaries. This weak-link behavior is assumed to be originated from a dirty grain boundary due to impurities and cracks. Although the J_c value gradually decreases with continuously increasing the applied magnetic field up to around 14 T, J_c value of 3.5×10^2 A/cm^2 can be maintained even at high magnetic field of 14 T. Zr doped samples exhibits J_c value of higher than 10^3 A/cm^2 maintained up to around 10 T. It is apparent that Zr doping was effective in increasing the irreversibility field.

From these difference $J_c - B$ behaviors, 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 A/cm^2. The following consideration was obtained: (1) Peak positions for pure Gd123 sample located at around $h = 0.3$ which was close to $h = 0.33$, suggesting that normal and point pinning are dominant [10]. As seen in SEM observation, fine Gd211 particles were dispersed after melting. (2)The case of 0.1 at% Zr sample, the peak position of 77 K locates at around $h = 0.5$, which is theoretically predicted for $\Delta\kappa$ pinning due to compositional fluctuations of $Gd_{1+x}Ba_{2-x}Cu_3O_y$ solid solution (Gd123ss) clusters with small x value. (3)Peak position $h = 0.4$, which is medium position of $\Delta\kappa$ pinning and normal

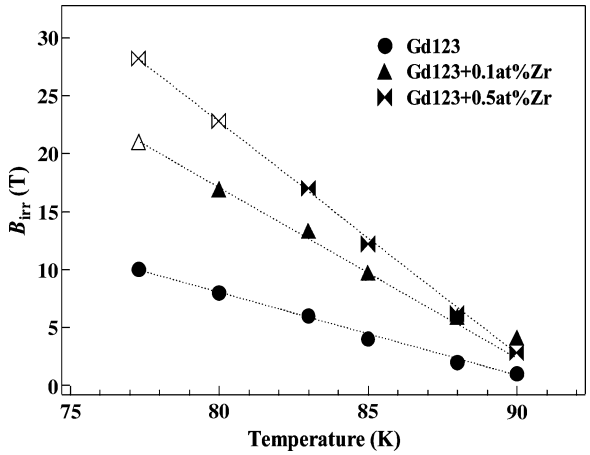

Fig. 4. The relationship between the irreversibility field and temperature for three kinds of Gd123 samples doped with Zr doping concentrations, 0, 0.1 and 0.5 at% Zr.

and point pinning, of 77 K for 0.5 at% Zr added sample 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 energy. Furthermore, Gd123ss clusters with lower T_c value may exist as normal particles at higher temperatures. It is also known that Ba is removed from the 123 matrix and preferably forms $BaZrO_3$ during heat treatment. Therefore, we consider that pinning contribution for Zr doped sample in the fields was owing to overlapping the field induced pinning such as Gd123ss clusters [11], and homogeneous distribution of Gd211 particles and nano-scale particles of Zr and/or Zr related compounds such as $BaZrO_3$ [8], [9].

Fig. 4 shows temperature dependence of the irreversibility field which is determined from the transport $J_c - B$ data. The irreversibility field of temperature lower than 80 K for 0.5 at% Zr and 0.1 at% Zr doped samples are extrapolated. There is clear enhancement of irreversibility field by Zr doping into Gd123, indicating flux pinning improvement. It is interesting that irreversibility field at 77 K may exceed 25 T by optimally Zr doping into Gd123 superconductors.

Although the J_c value in a zero magnetic field was decreased by Zr doping, we could observe the enhancement of J_c in magnetic field. Because of clarification of the pinning mechanisms in magnetic fields is a far more complicated problem, it is difficult to discuss precisely the dominant pinning contribution from only these experimental results. Anyway, it needs to be accompanied by an optimized amount of a fine secondary phase and both refinement and homogeneous dispersion of them. To obtain higher J_c value, we are under investigation how nano-scale inclusions form during heat treatment, what kinds of pinning act and pinning mechanism for filamentary Gd123 in high magnetic fields.

IV. Conclusion

The effect of Zr doping on transport critical current density and microstructure of filamentary Gd123 superconductor processed via chemical route was investigated. Maximum J_c value of 2.5×10^4 A/cm^2 at 77 K and 0 T for the pure Gd123 sample was obtained, contrast to the J_c values of the sample with 0.1at% Zr and 0.5 at% Zr doping were 2.0×10^4 A/cm^2 and 8.2×10^3 A/cm^2, respectively. The sample doped with 0.1 at% Zr exhibited stacking microstructure, in which fine Gd211 particles with mean diameter of about 0.5 μm were homogeneously dispersed. From J_c measurement in an applied magnetic field, the J_c value of Zr free sample gradually decreased with increasing applying fields and the superconductivity was disappeared around 10 T. Comparing with pure Gd123, a J_c value higher than 10^3 A/cm^2 was maintained up to 10 T for both 0.1at% Zr and 0.5 at% Zr doped samples. In conclusion, Zr chemical doping to Gd123 was found to be effective in homogeneous dispersion of Gd211 and reduction of the size of Gd211 particles. Furthermore, experimental results indicate that small amount of Zr doping is an important factor for enhancement of the irreversibility field.

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