Microstructural Analysis of Superconducting Joint Fabricated Using CJMB Between Gd123-coated Conductors

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Xinzhe Jin, Yasuteru Mawatari, Toshihiro Kuzuya, Yusuke Amakai, Yoshinori Tayu, Naoki Momono, Shinji Hirai, Yoshinori Yanagisawa

***Abstract*— A superconducting joint between two Gd123-coated conductors was successfully formed using crystal growth in the bulk (CJMB). An intermediate Yb123 layer was used at the junction, and was melted to form a joint by heat treatment at a temperature below the melting point of the RE123 (such as Gd123) in the coated conductor. This liquid-phase bonding results in high tensile strength, which has exceeded 100 MPa in previous studies. Nevertheless, the joint principle has not been sufficiently clarified. In this study, we performed microstructural analysis of the joint using X-ray diffraction and scanning electron microscopy combined with energy-dispersive X-ray spectroscopy to form a clearer understanding of the joint formation mechanism in order to achieve a high critical current in the junction.**

***Index Terms*— joint interface, Gd123, coated conductor, Yb123**

I. Introduction

RARE-EARTH (RE)-based cuprate superconductors such as $REBa_2Cu_3O_{7-\delta}$ (RE123, RE: rare-earth element, δ = 0–0.2) have allowed the development of high magnetic field superconducting magnets with high operating currents [1-2]. Currently, RE123-coated conductors with critical currents above 200 A at 77 K are commercially available [3]. Longer coated conductors are under development [4-6], but the maximum length in current research and development is on the order of 1 km. Unfortunately, this length is insufficient for general-use magnets, which can require several kilometers of coated conductor as insert coil. Thus, it is necessary to develop a method for producing a low-resistance joint between two coated conductors. In particular, such joints are essential for applications such as nuclear magnetic resonance and magnetic resonance imaging [7,8], where consistently high sensitivity and resolution are required, without the influence of noise induced by the power supply.

A joining method based on partial melting was reported by Park et al., in which a joint was produced by direct contact without any intermedium [8]. The joint exhibited superconducting behavior with a high critical current.

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We subsequently proposed a joining method which we refer to as crystalline joint by melted bulk (CJMB) [9]. In this method, a thin layer of Yb123 is used and melt-grown at boundary in high temperature. The joint can be fabricated in a relatively short time of about 11 h (including oxygen annealing for 10 h). Joints fabricated by such liquid-phase growth have exhibited tensile strengths exceeding 100 MPa [9,10], in addition to superconducting behavior. However, the critical current was only about 10 A, which was about 20 times less than that for the original coated conductor.

Recently, joints exhibiting a critical current above 100 A (compared to 200 A for the original coated conductor) at 77 K were reported by Ohki et al. using intermediate grown superconducting (iGS) method [11]. In this method, a joint between RE123-coated conductors was prepared using a microcrystalline Gd123 precursor intermediate layer and a joint strap to increase the mechanical strength.

Although a superconducting joint was achieved, the joint formation mechanism has not been sufficiently clarified. It is therefore necessary to investigate the microstructure at the joint interface to obtain a better understanding. For example, what kind of compounds or elements form the superconducting junction, and how do they affect the critical current? These are important questions for achieving future improvements in the critical current and mechanical strength.
In the present study, joints were prepared using the CJMB method and were evaluated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and electrical measurements.

II. Experimental

A. Sample Preparation

A 4-mm-wide Gd123-coated conductor fabricated by Sumitomo Electric Industries, Ltd. was used for joining. The thicknesses of Gd123 and buffer layers are 3-4 μm and 0.4 μm, respectively. The substrate consist of 2 μm thick Ni (under buffer layer), 17 μm thick Cu, and 100 μm thick stainless steel layers. The thickness of silver layer on the Gd123 layer is 2 μm, and that for copper on each side is 20 μm (40 μm for thickness direction of tape). The critical current and *n* value is 200 A and 28, respectively. The partial Cu and Ag layers about 4 cm length were removed by etching using dilute

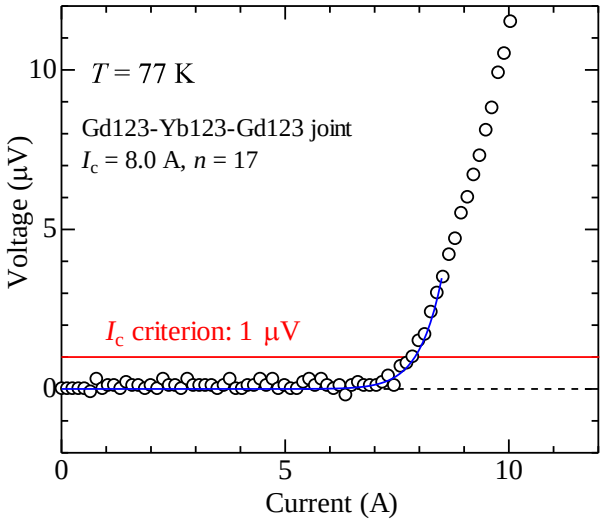


Fig. 1. *I-V* characteristics of joint sample. The solid line indicates 1 μV, corresponding to the criterion of critical current in this study.

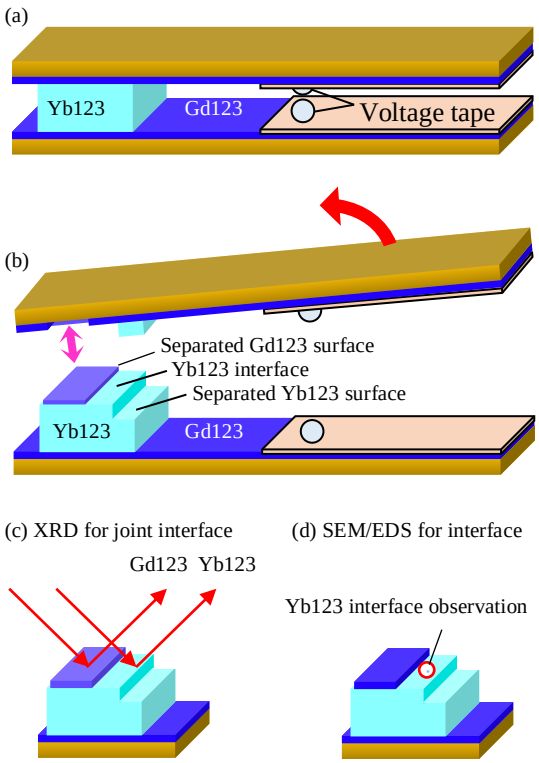


Fig. 2. Schematic illustrations of sample preparation and measurement methods: (a) joint sample, (b) joint interface exposure for measurements, (c) XRD measurement, and (d) SEM/EDS analysis of interface.

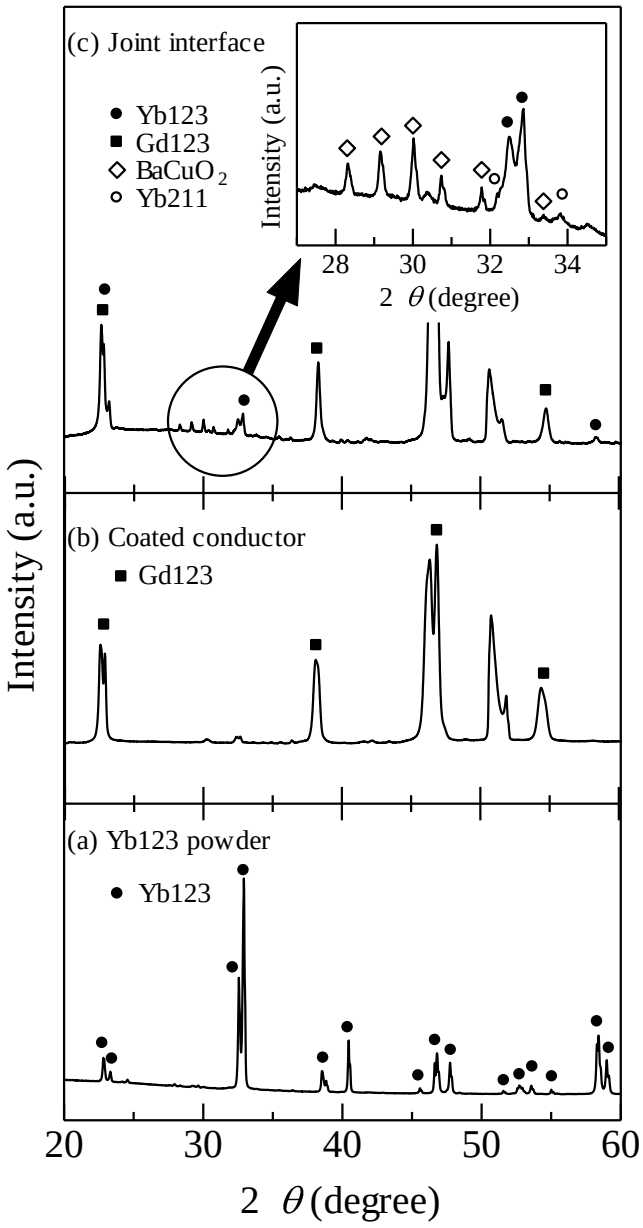
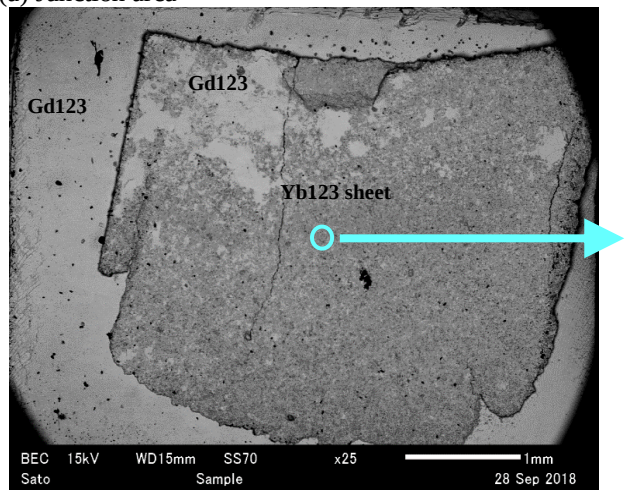


Fig. 3. XRD patterns for samples. The inset shows an expanded view of the region between 27 and 35°. The unmarked peaks are those from the buffer and the substrate layers.

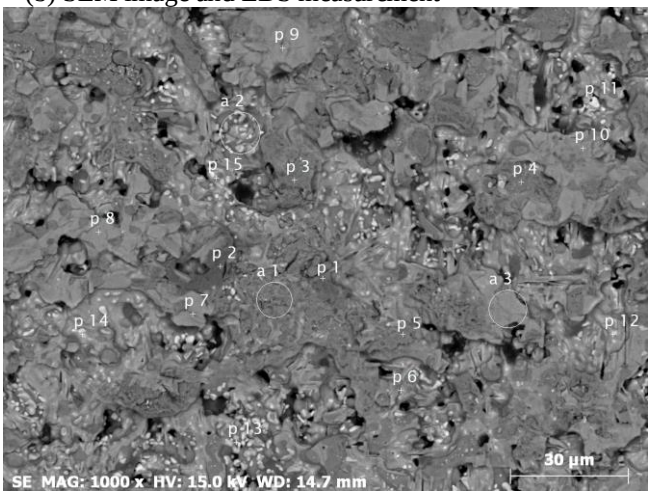
sulfuric acid, hydrogen peroxide, and citric acid. A 1-mm-thick polycrystalline Yb123 plate was prepared by sintering, and was ground to a thickness of 0.1 mm using sandpaper to serve as the intermediate layer.

The heating length is about 1 cm at the end of sample, and the highest temperature of unetched Cu layer 4 cm away from the melting zone was below 373 K. Heat treatment was performed at 1203 K for 1 min by heating rate of 100 K/min without pressing in an oxygen gas atmosphere of 0.5 atm., followed by annealing at 723 K for 10 h with cooling rate of 10 K/min in an oxygen gas atmosphere of 1 atm. The proportional–integral–derivative (PID) temperature control was performed by using type R thermocouple set near the center of heating length of sample. The *I-V* properties were measured at 77 K, and the critical current I_c was 8.0 A with an n value of 17, as shown in Fig. 1. Figure 2(a) shows a schematic illustration of the joint. The length and thickness (at junction) of joint are 10 cm and 0.3 mm, respectively. The

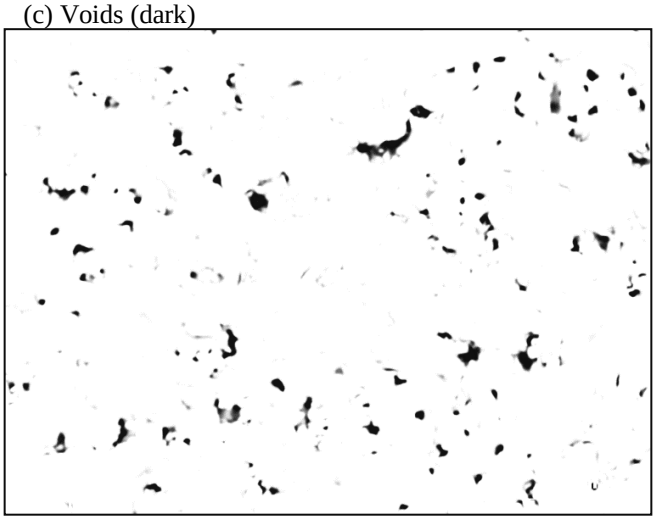
(a) Junction area



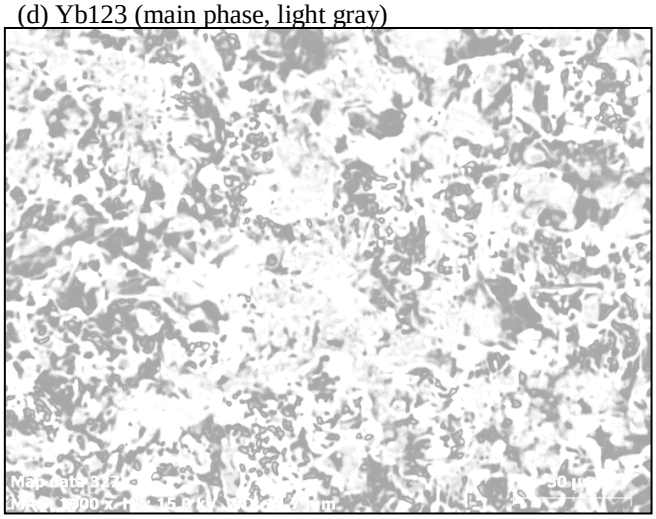
(b) SEM image and EDS measurement



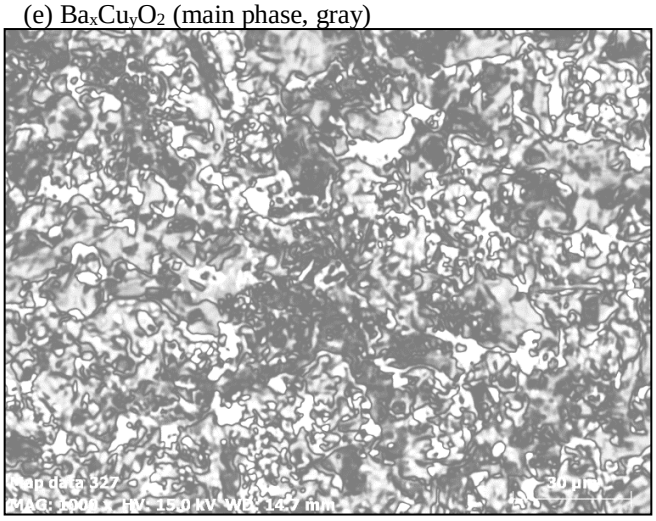
(c) Voids (dark)



(d) Yb123 (main phase, light gray)



(e) $Ba_xCu_yO_2$ (main phase, gray)



(f) CuO (dark gray)

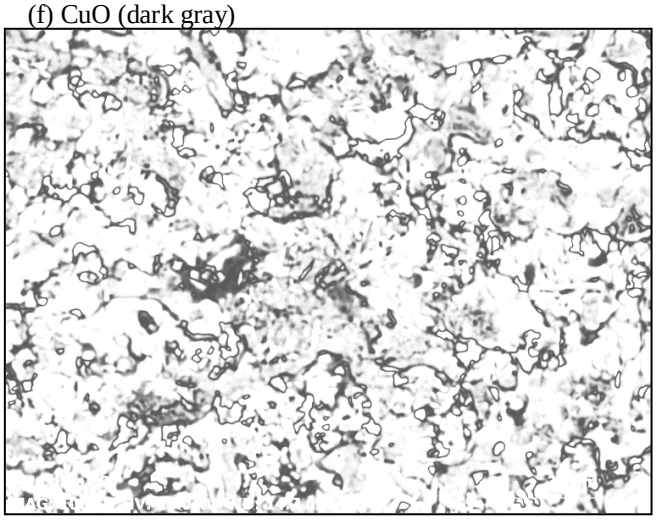


Fig. 4. SEM images and qualitative results of EDS mapping. (a) joint interface at 25× magnification, (b) Yb123 surface at joint interface at 1000× magnification, (c) distribution of voids, (d) distribution of mainly Yb123, (e) distribution of $Ba_xCu_yO_2$ (liquid during the joining process), and (f) distribution of CuO.

distance between two voltage taps each soldered on the Cu layer is 10 cm, as shown in the figure.

To observe the joint interface after *I-V* measurements, one side of the coated conductor was delaminated by peeling, as shown in Fig. 2(b). Thus, the Yb123 interface at the joint was exposed, with Gd123 and Yb123 surfaces separated inside

each material. Finally, the sample was shortened by cutting off the coated conductor for XRD and SEM/EDS measurements.

B. Measurements

A 9 kW Cu-Kα beam was chosen by using the SmartLab X-ray diffractometer manufactured by Rigaku Corporation. XRD measurements were carried out at room temperature for several minutes in the 2θ region of 20–60°. The measurement method is shown in Fig. 2(c). Since no shield plate was used, the Gd123 layer and Yb123 surfaces were detected. For comparison, Yb123 powder and a Gd123-coated conductor following Cu and Ag removal were also measured.

SEM manufactured by JEOL Ltd. (TSM-6510) was used in this study. SEM/EDS measurements were performed at the Yb123 interface, as illustrated in Fig. 2(d). SEM images enlarged by 25 and 1000 times were obtained. For the latter, an EDS compositional analysis was carried out at multiple points and areas that differed in grayscale intensity. Distribution maps were then created for each compound.

TABLE I
EDS ANALYSIS RESULTS FOR SELECTED POINTS AND AREAS

Point/area	Yb (at.%)	Ba (at.%)	Cu (at.%)	Estimated compounds	Color
p1	0	33	67	$Ba_xCu_yO_2$	gray
p2	0	2	98	CuO	dark gray
p3	0	61	39	$Ba_xCu_yO_2$	gray
p4	0	39	57	$Ba_xCu_yO_2$	gray
p5	0	57	42	$Ba_xCu_yO_2$	gray
p6	12	40	49	—	—
p7	0	38	59	$Ba_xCu_yO_2$	gray
p8	13	33	54	—	—
p9	5	37	58	—	—
p10	6	41	53	—	—
p11	43	25	32	Yb211	white
p12	18	32	50	Yb123	light gray
p13	32	20	48	—	—
p14	31	27	42	—	—
p15	15	51	34	—	—
a1	0	43	54	$Ba_xCu_yO_2$	gray
a2	18	33	49	—	—
a3	10	37	52	—	—

III. Results and Discussion

A. XRD patterns of the samples

Figure 3 shows the measured XRD patterns. From Fig. 3(a), the original Yb123 powder was almost single-phase. The Gd123 phase in the original coated conductor appeared to be well textured as 00L reflections dominate the XRD pattern (Fig. 3(b)). For the joint interface in Fig. 3(c), Yb211 and $BaCuO_2$ were detected in addition to the above two phases, as shown in the inset figure. This indicates that the Yb123 phase separated by incongruent melting to generate a solid Y211 and liquid Ba-Cu-O system. The Ba:Cu composition ratio can deviate slightly from 1:1 in the Ba-Cu-O system, so the notation $Ba_xCu_yO_2$ was used in this study. Considering the composition ratio of Yb123, CuO may also be present in very small amounts, even though it was not observed in the XRD profiles.

B. SEM/EDS analysis of joint sample

An SEM image of the joint interface is shown in Fig. 4(a). Both the Gd123 and Yb123 surfaces were observed, and the center of the Yb123 joint interface was imaged at a magnification of 1000×, as shown in Fig. 4(b). Many small voids were scattered about the interface. To clearly illustrate the distribution of these voids, they are shown as dark regions in Fig. 4(c). These may act as beneficial oxygen pathways during annealing.

In Fig. 4(b), a total of 15 points and 3 areas were chosen for EDS analysis, and the obtained elemental contents are listed by atomic percent in Table 1. Next, the compounds determined by the XRD analysis along with the potentially present compound CuO were identified at some points, and the grayscale intensity was recorded in each point. At points p1, p2, p3, p4, p5, p7, and area a1, no Yb exists, but the gray $Ba_xCu_yO_2$ phase is present. For points p11 and p12, the compositional ratio is similar to that for Yb211 (white) and Yb123 (light gray), respectively, indicating that only a single phase is present. A single compound is not obtained at points p6, p8, p9, p10, p13, p14, p15, and in areas a2, a3. Considering the low intensity of the Yb211 XRD peaks in Fig. 3, its content is lower than that of Yb123. Therefore, the light gray area is primarily the Yb123 phase, which is shown separately from the original Fig. 4(b) in Fig. 4(d). The gray phase was assumed to contain mainly $Ba_xCu_yO_2$. The distribution is shown in Fig. 4(e), and covers a large area, indicating a sufficient amount of liquid at the joint interface to achieve a high bonding strength. Figure 4(f) shows the distribution of CuO, and it almost draw curved lines like contour of $Ba_xCu_yO_2$ or Yb123 or voids.

In the joint with CJMB method, the critical current of joint depends on the cross-section of bulk that current flows the Y123 phase in cross-section, as shown in Fig. 4 (d). As seen in the figure, the current area of Yb123 is about 20-30% of entire area, and it is necessary to increase the Yb123 area to improve the critical current of joint. In this study, we found that the Yb123 area is small and it is a major reason of the small critical current of joint in current study. This issue should be solved for development of joint with high critical current in future.

IV. Conclusion

Using the CJMB method, we have prepared a superconducting joint between Gd123-coated conductors to study the microstructure at the joint interface. In the XRD patterns, Gd123, Yb123, Yb211, and $BaCuO_2$ phases were detected at the joint interface, indicating that incongruent melting occurred during the joint formation process. At the joint interface, SEM/EDS analyses were performed and the compounds observed in the above XRD measurements were assigned to different colored regions in the image. Then,

distribution maps for each compound were obtained. The distribution of Yb123 showed multiple junctions separated by regions of $Ba_xCu_yO_2$ and CuO.

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