3D microstructure and critical current properties of ultra-fine-grain Ba(Fe,Co)₂As₂ bulk superconductors

Yusuke Shimada (✉ yusuke.shimada.e1@tohoku.ac.jp)

Tohoku University

Shinnosuke Tokuta

Tokyo University of Agriculture and Technology

Akinori Yamanaka

Tokyo University of Agriculture and Technology

Akiyasu Yamamoto

Tokyo University of Agriculture and Technology

Toyohiko. J Konno

Tohoku University

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Abstract

In iron-based superconductors, randomly oriented grain boundaries have a strong influence on the transport properties via intrinsic weak-link and flux pinning mechanisms. Herein we report the critical current density (J_c) and the three-dimensional microstructure of polycrystalline bulk Co-doped Ba122 superconductors, with highly dense grain boundaries (grain size smaller than 50 nm), produced by high-energy milling. Three-dimensional electron microscopy revealed that the anomalous growth of secondary particles (aggregation) and the inter-aggregation structures were significantly different in the samples with finer grains, which may have extrinsically limited J_c . These important microstructural features were quantified as two parameters—local thickness and total pore length—by reconstructing the three-dimensional structure of the superconducting phase using the adaptive thresholding method. The results obtained in this study suggest that understanding and controlling the microstructural formation process by sintering are instrumental for improving the J_c properties of 122 polycrystalline materials consisting of ultrafine grains.

Introduction

Certain groups of iron-based compounds have been developed as high-temperature superconductors [1]. Among them, the AE-122 series, with AEFe_2As_2 composition (AE: alkaline earth metal), has a transition temperature (T_c) of 38 K [2] and an upper critical field stronger than 50 T [3, 4]. Therefore, it should be used as a high-field magnet. In addition, the electromagnetic anisotropy, γ , of AE-122 [3, 5] is lower than that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) [6]. A high critical current density (J_c) of over 10^5 A cm^{-2} at 4.2 K has been reported in Ba-122 polycrystalline wires fabricated by the powder-in-tube process [7-10]. In comparison, the critical current density of AE-122 exceeds 10^6 A cm^{-2} at 4.2 K [11-13] or 16 K [14] in the self-field in a thin film with a controlled microstructure. Thus, controlling the internal structure of the polycrystal AE-122 is required to extract the potential of the material.

The transport and critical current properties of polycrystalline superconducting materials strongly depend on their microstructures. In previous studies, we selected a few factors pertaining to the microstructures and discussed their relationship with the critical current property. In particular, the grain boundary is crucial to the transport properties, especially the critical current of polycrystalline superconducting materials. Several studies on grain boundary characteristics have been conducted [15-17]. For example, in metallic superconductors like MgB_2 and Nb_3Sn , the critical current properties are improved by grain refinement, because grain boundaries are known to act as pinning centers of magnetic flux [15, 16]. Meanwhile, in copper oxide-based superconductors like YBCO, the grain boundaries with an orientation difference greater than $2-3^\circ$ show weak links and thus, significantly reduce the critical current [17]. High critical current has therefore been achieved in YBCO by growing nanorods on single-crystal thin films to introduce artificial pinning centers [18] and in Bi-based superconducting materials by fabricating wires with a c -axis orientation that has no tilt angle component with respect to the ab plane [19].

Iron-based superconductors also have inherently weak links [20-22]. Previous studies have shown that the transport critical current in Fe (Se,Te) decreases to approximately 1/5th–1/4th at a misorientation angle of 15° compared to that at 0° and further decreases by an order of magnitude at 25° [21-25]. In our previous study, we found a correlation between the improvement in critical current characteristics and the reduction in grain size by microstructural analysis using electron microscopy [26]. The enhancement in critical current can be explained by the flux pinning model or the Josephson junction model [27]. A fundamental concern regarding the application of iron-based superconductors is the extent to which an increase in grain boundary area per unit volume would lead to an increase in J_c .

In this study, we prepared Co-doped Ba-122 polycrystalline bulks, with grain sizes less than 50 nm, by a high-energy milling process and attempted to identify and quantitatively extract the microstructural factors governing the transport properties of polycrystalline bulks. Since the transport current flows three-dimensionally, it is difficult to obtain accurate data using only conventional two-dimensional observations. Therefore, we utilized macro-scale three-dimensional microstructure observations as an evaluation technique. Three-dimensional microstructures are important in many bio-, structural, and functional materials as well. Three-dimensional microstructure observation is carried out by several methods [28-30], among which, we have chosen and used the serial sectioning method, which involves the use of scanning electron microscope (SEM) equipped with a focus ion beam (FIB) mill and has a high spatial resolution to extract materials from the micrometer scale to 10–100 nm [28]. We adopted image processing with OpenCV to remove the artifacts that arise because of the complex contrasts in the background, as well as those originating from the material, during the analysis. Thus, in this study, we discovered and quantitatively extracted two new parameters related to grain connectivity.

Results

Table 1 lists the properties of the fabricated bulk material. With increasing E_{BM} , the unit cell parameters, a and c -axes, and T_c monotonically increase and decrease, respectively, because of the increase in mechanical strain due to the increase in E_{BM} . The maximum value of J_c is obtained for the bulk fabricated at $E_{BM} = 80$ MJ/kg, from which it decreases with increasing E_{BM} . Figure 1 shows the transmission electron microscopy-bright field (TEM-BF) images, from which the average grain sizes have been measured, and the electron diffraction patterns of the bulk samples. The electron diffraction patterns show that the main phase of all the bulk samples is Ba-122. The ring diffraction pattern indicates that there is no ordering in the crystal orientation, suggesting that the bulk material has almost a random orientation.

Figure 2 shows the correlation between E_{BM} and grain size or J_c . The grain size tends to decrease with increasing E_{BM} , and it is less than 50 nm for the samples fabricated at an E_{BM} greater than 230 MJ/kg; this indicates that the bulk material has a much finer polycrystalline nature than the previous Ba-122 bulks. The inset of Fig. 2 shows the correlation between the inverse grain size and J_c for the specimens prepared with E_{BM} greater than 80 MJ/kg. The J_c values decrease for the fine-grained bulks. In our

previous study, the J_c values increased with increasing inverse grain size of Ba-122 [27]. These results show that J_c decreases with reduction in grain size at a threshold of 80 MJ/kg E_{BM} , and this decrease may be caused by internal structures.

Figure 3 (a) shows a high angle annular dark field–scanning transmission electron microscopy (HAADF–STEM) image of the bulk that was fabricated at 590 MJ/kg E_{BM} . There are three phases in the bulk; Ba-122, Fe–Co–As-rich, and Ba–O-rich, as shown in the energy-dispersive X-ray spectroscopy (EDS) map in Figure 3 (b)–(f). The Fe–Co–As-rich phase has a grain size of 20–100 nm, which is similar to that of Ba-122, and is mixed in the Ba-122 phase; whereas the Ba–O-rich phase is coarse (500–1000 nm) with an indefinite shape that fills the gaps between the Ba-122 phases. On the other hand, these phases are hardly observed in the bulk fabricated at 80 MJ/kg E_{BM} . A possible reason for the decrease in J_c in the bulk fabricated at 590 MJ/kg E_{BM} is the decrease in the volume fraction of the Ba-122 phase due to the formation of these secondary phases. The volume reduction rate is estimated, from Figure 3, to be approximately 10%–15% for the bulk fabricated at 590 MJ/kg E_{BM} , where the secondary phases are the most prevalent.

The effects of E_{BM} on the macroscale structures were investigated. Figure 4 shows the three-dimensional and typical cross-sectional SEM-secondary electron (SE) images of the bulks fabricated with E_{BM} of 80 MJ/kg [(a) and (c)] and 230 MJ/kg [(b) and (d)]. Both the bulks have a macroscale structure with pores surrounding the aggregated polycrystals, which are coarser than the grains. For the 80 MJ/kg bulk, which has a high transport current, the pores are discrete and the Ba-122 aggregates are generally bonded with each other, whereas for the 230 MJ/kg bulk, the pores are continuous and the aggregate bonding area appears to be narrow. This is also evinced by the cross-sectional SEM image, especially at the neck of the aggregate bonding (Figures 4 (c) and (d)), which is expected to be a macroscale structural singularity. Table 2 shows a comparison of the extracted macroscale structural parameters related to the transport current and the aggregate bonding at the neck. The extracted parameters, which were measured from the three-dimensional reconstruction images, are the volume fraction, local Ba-122 phase thickness, which is the total value of aggregate area and neck area, and total path length of the connected pore. Figures 4 (e) and (f) show the examples of the local thickness measurements. First, the vertices are detected as a triangle mesh from the segmented Ba-122 images for reconstruction, following which, at each edge, an inscribed sphere is drawn such that the largest diameter does not encompass the other edges. Subsequently, the diameter is defined as the local thickness value, which includes the frequency and area of the neck. The total length of a pore per volume is estimated by normalizing the sum of the maximum lengths at each pore after segmentation by the watershed algorithm for the pore with the reconstruction volume. The results show that there is nearly no difference in the volume fraction between the two bulks. In contrast, the maximum local thickness of Ba-122 is higher in the 230 MJ/kg bulk, although the average thickness is higher in the 80 MJ/kg bulk. Furthermore, the total path length of the connected pores is

shorter in the 80 MJ/kg bulk. These results indicate that the path length is shorter for the 80 MJ/kg bulk, even though the total volume of the pores in the two bulks is equal, i.e., these parameters indicate that the pores are discrete in 80 MJ/kg bulk, which is consistent with the observation results. It is considered that the local thickness of Ba-122 reflects the area at the neck of the aggregate, whose nanoscale structure is shown in the TEM-BF image (Figure 5). In the neck part, there are a few grains that contribute to the aggregate bonding, which is considered the limiting factor of the transport current. These results suggest that the bonded area of the aggregate should be considered the factor responsible for the decrease in J_c despite the grain size reduction in the bulk of 230 MJ/kg.

Discussion

The results of the microstructural observations suggest that there are differences in both the intra-aggregate structures, such as grain size and size of the secondary phases, as well as the inter-aggregate neck structures with increasing ball milling energy. These factors influence the transport properties and J_c via connectivity [31], which depends on microstructural defects and grain boundaries.

We now discuss the microstructure formation process on the basis of present findings. The intra-aggregate structures had ultrafine grains and a distribution of secondary phases. The grain refinement is considered to occur because of the strain energy from high-energy ball milling. In particular, for E_{BMS} of 80 MJ/kg or more, the high strain energy results in the formation of many crystal nuclei during mechanical alloying. In addition, the sintering temperature of 600 °C is not sufficient to cause a significant grain growth in Ba-122, which has a melting point of 1300 °C [32]. The result is expected to be an ultrafine grain smaller than 100 nm. Moreover, the formation of Ba–O and Fe–Co–As enriched phases as the secondary phases in the aggregates was observed. Several previous studies have reported similar phases in Ba-122 bulks that were fabricated in a glove box [10, 25]. Therefore, even at a low temperature of 600 °C, phase separation may have occurred owing to the loss of Ba atoms from the grain surface. Furthermore, as the grain size decreased, the grain surface area increased, thereby promoting the formation of the secondary phase. The unusual structure of inter-aggregates is the neck, and the following points discuss the formation of pores surrounding the neck. Pores can be generated by: (1) dissolution of Ba due to the reactions during sintering, (2) pores formed by powder filling during initial pellet fabrication, or (3) migration of pores, which existed from the initial stage of sintering, from within the aggregate to between aggregates, i.e., these pores were formed before or at the beginning of the sintering. Even in high-energy ball-milled bulks, sintering promotes densification in the aggregates, which results in less mass diffusion transfer between the aggregates, suggesting that the pores are not filled and remain. In particular, at $E_{\text{BMS}} > 230$ MJ/kg, the maximum local thickness of Ba-122 is high, indicating the formation of dense and coarse aggregates, while insufficient grain growth may have resulted in a narrowing of the neck.

From the discussion, it can be inferred that the simple ball milling process can control the grain size to 10-nm level, which is useful for future microstructural design of iron-based superconducting materials. On the other hand, the discussion suggests that the neck of the aggregate bonding needs to be extended to improve J_c further. Hot isostatic pressing sintering [33] and spark plasma sintering to melt the neck under a high-pressure environment are a few possible methods to achieve the extension of aggregate bonding neck. In addition, the results of our study show that these microstructural parameters were successfully quantified in three dimensions and that the degree of microstructural control in Ba-122 can be organized as quantitative values in the future.

Conclusion

In this study, we quantitatively identified the microstructural factors that affect the transport properties of Co-doped Ba-122 ultrafine grain polycrystalline bulk using three-dimensional observation. The results show that the grain size decreases with increasing ball milling energy, and ultrafine-grained Ba-122 bulk with the dimensions at a scale of 10 nm can be fabricated. However, in the macroscale structure, it was suggested that the narrowing of the junction neck between the aggregates due to the increase in ball milling energy blocked the transport current. In addition, we succeeded in quantifying the three-dimensional structure obtained by serial sectioning and were able to derive two parameters, viz. the local thickness of Ba-122 and the total path length of the pore, indicating the effectiveness of this analysis as an evaluation method for structural control.

Methods

Co-doped Ba-122 bulk samples were prepared by the following sequential steps. Pure metal powder with a nominal composition of $\text{BaFe}_{1.84}\text{Co}_{0.16}\text{As}_2$ was mechanically alloyed by a ball-milling process. The ball-milling energy, E_{BM} , which is a function of the milling duration and the number of rotations [24], was systematically varied as 50, 80, 230, and 590 MJ/kg. Compacted, alloyed powder samples were sintered at 600 °C for 48 h under vacuum [34]. The lattice parameter of the obtained bulk was measured by X-ray diffraction (D2 PHASER, Bruker, MA, USA) and the critical current density J_c was obtained from magnetization measurements using a superconducting quantum interference device (SQUID) and vibrating sample magnetometer (VSM) (MPMS3, Quantum Design Inc., CA, USA). The transport properties were determined using the conventional four-probe method. T_c was defined as 90% of the superconducting transition temperature of electrical resistivity.

The multiscale structures were observed using various electron microscopy techniques. The macroscale structures, such as the connection of aggregates, were analyzed by SEM (Versa 3D, Thermo Fisher Sci., MA, USA), whereas the nanoscale structures, such as grain size and phase distribution, were analyzed by TEM (ARM-200F, JEOL Ltd., Japan) and EDS. Three-dimensional observations were performed using the serial sectioning method using FIB-SEM, after which, the sample was polished with Ga^+ ions, and the slice width was set to 20 nm. For three-dimensional image analysis, the obtained cross-sectional SEM

images were first binarized. However, images obtained by SEM often have different luminance distributions at each small region of the image and thus, simple image thresholding with the use of single threshold value may not be appropriate. In this study, we used the adaptive thresholding method, which is an advanced image thresholding method that uses different threshold values for each small region in the image. We developed a Python code that implements the adaptive threshold function of the OpenCV library using `cv2.ADAPTIVE_THRESH_GAUSSIAN_C`. The adaptive thresholding used in this study is

$$dst(x, y) = \begin{cases} L_{\max} & \text{if } src(x, y) > T(x, y) \\ 0 & \text{others} \end{cases} \quad (1)$$

expressed by the following equation:

where $dst(x, y)$ is the binary value, while $src(x, y)$ is the luminance value (i.e., from 0 to 255) of the 8-bit grayscale input image at the pixel coordinates (x, y) . $T(x, y)$ is the threshold of the luminance values in pixel coordinates (x, y) of the input image, which is calculated as follows: $T(x, y)$ is the difference of the Gaussian weighted sum of the neighborhood values and the constant C , where the size of the neighborhood area is $N \times N$ pixels. In equation (1), $L_{\max}$ is the luminance value at the pixel coordinates satisfying the condition of equation (1). In this study, the original images obtained by SEM were smoothed with a median filter, and each filtered image was used as the input image for adaptive thresholding. We used $L_{\max} = 255$, $N = 111$, and $C = 15$, and the binarized images were stacked during alignment to obtain a three-dimensional reconstructed image.

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Declarations

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Tables

Table 1 Properties of bulks

E_{BM}	Sintering conditions		a -axis	c -axis	J_c at 5K in sf	T_c^{res}
[MJ·kg ⁻¹]	[°C]	[h]	[Å]	[Å]	[x 10 ⁴ A·cm ⁻²]	[K]
50	600	48	3.9604	12.997	1.37	26.6
80	600	48	3.9596	13.004	1.71	26.4
230	600	48	3.9598	13.013	0.366	26.0
590	600	48	3.9588	13.013	0.233	25.1

Table 2 Structural parameters of bulks obtained from three-dimensional images

E_{BM} [MJ·kg ⁻¹]		80	230
Volume fraction [%]		84.58	82.06
Local thickness of Ba122 [μm]	Ave.	0.70	0.58
	SD	0.35	0.31
	Max	2.7	3.2
Total length of connected pore [μm ²]		23.0	32.9

Figures

Figure 1

TEM-BF images and electron diffraction patterns of bulks fabricated at 50(a), 80(b), 230(c) and 590(d) MJ/kg of EBM. The average grain sizes of Ba-122 are 500, 140, 50 and 30 nm, respectively.

Figure 2

The relationship between EBM and J_c (left) and grain size (right) of Ba-122. The inset shows the dependence of J_c on the inverse grain size. J_c obtained at 5 K in self-field.

Figure 3

HAADF-STEM image (a) and elemental distribution maps of Ba (b), Fe (c), Co (d), As (e) and O (f) of Ba-122 bulk prepared at 590 MJ/kg of EBM.

Figure 4

Three-dimensional and typical cross-sectional SEM-SE images of the bulks fabricated with EBM of 80 MJ/kg ((a) and (c)) and 230 MJ/kg ((b) and (d)). The example of method for measurement thickness of two-dimensional slice image (a) and three-dimensional reconstructed image of the bulk EBM of 80 MJ/kg. The arrows in (c) and (d) show the necks between the aggregates.

Figure 5

A TEM-BF image of a neck structure in EBM of 590 MJ/kg.