Title: Microstructural connectivity in sintered ex-situ MgB₂ bulk superconductors

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Abstract

We have performed combined high-resolution microstructural and grain orientation analyses to understand the key microstructural factors associated with high intergranular transport current in polycrystalline bulk forms of MgB₂. The ex-situ method can produce MgB₂ with relatively high packing factors; nevertheless, the connectivity of MgB₂ fabricated by the ex-situ method (ex-situ MgB₂) was less than that of in-situ MgB₂. The poor connections between MgB₂ grain aggregates cause the low connectivity of ex-situ MgB₂. Plate-like pores are present between the aggregates of MgB₂ grains in ex-situ MgB₂; these pores remain even after prolonged self-sintering at high temperatures. In addition, MgB₂ crystals decompose to MgB₄ in sintering for a long period. Moreover, MgO particles are formed between MgB₂ grain aggregates and inhibit interaggregate connections. In contrast, in-situ MgB₂ fabricated at the same sintering conditions exhibits spherical pores between MgB₂ grains, resulting in a uniform pore distribution and intergranular connection. These problems must be addressed to further enhance the connectivity in ex-situ MgB₂.

1. Introduction

The superconducting transition temperature of MgB_2 ($T_c = 40 \text{ K}$) is higher than that of other metallic superconductors [1]. MgB_2 is therefore expected to be useful at medium temperatures, i.e., approximately 20 K, that can be reached by compact cryocoolers. In addition, MgB_2 does not exhibit the problem of weak links between the misoriented crystal grains [2] because the MgB_2 coherence length $\xi = 5.2 \text{ nm}$ [3] is greater than that of cuprate and iron-pnictide superconductors [4, 5]. Therefore, MgB_2 can be used in a randomly oriented polycrystalline form that can be easily fabricated by various techniques [6-9].

There are two common methods for fabricating MgB_2 bulks and wires. The first method is by using an in-situ reaction that starts with the heat treatment of mixed Mg and B powders. It is easy to add impurities to improve flux pinning in the in-situ method [10-12]. However the packing factor (P) of MgB_2 fabricated by the in-situ method is low at approximately 50% due to the melting of Mg [13]. The low P value corresponds to low connectivity (K); since the connectivity specifies the effective cross-sectional area that can contribute to the transport current, low P values are unfavorable [14]. Moreover, large B grains remain in the microstructures formed by the in-situ method, and these grains also decrease the connectivity [15, 16]. The B grain size is also effective to control critical current property and core structure [17, 18].

The ex-situ method is the second approach for fabricating MgB_2 bulks and wires [19-25]. In this method, pre-reacted MgB_2 powders are cold-worked and heated. Therefore, no pores are formed by Mg melting during the heat treatment, and higher packing factors can be expected compared to those observed for the in-situ method. Although the packing factor is higher for the ex-situ synthesized MgB_2 , its connectivity was found to be equal to or even less than that of the in-situ fabricated MgB_2 with an identical packing factor [26]. This is presumably because the adhesion of MgB_2 grains in ex-situ synthesized MgB_2 is weak even after sintering at a high temperature of approximately 1100 °C [21].

Self-sintering is a technique for the densification and strengthening of the intergranular connections of

metals, alloys, and ceramics. Since the atomic diffusion for self-sintering is promoted by higher temperatures, the self-sintering of ceramics and alloys is usually performed near the melting point [24, 27]. While the MgB_2 melting point is approximately 2300 °C, the boiling point of Mg and the decomposition point of MgB_2 are approximately 1090 °C and 1545 °C (under 1 atm), respectively [28]. The lower temperatures of these processes make it difficult to sinter MgB_2 at temperatures near the melting point, necessitating the use of additional methods such as hot pressing [29, 30], hot isostatic pressing [31, 32], and spark plasma sintering [33-35] to achieve dense and well-connected grain boundaries in ex-situ MgB_2 bulks and wires.

The application potential of dense ex-situ MgB_2 would be much enhanced if the self-sintering of MgB_2 can be promoted at reasonable temperatures without high pressure. Recently, Tanaka *et al.* reported that prolonged sintering at 900 °C promotes the self-sintering of MgB_2 grains under ambient pressures [36]. A high connectivity exceeding 20% was obtained due to the improved intergranular coupling at the boundaries of sintered grains, with a high packing factor of approximately 75%. However, the reported connectivity became still lower than that expected from the in-situ MgB_2 with an identical packing factor.

In this study, we performed comparative evaluations of the microstructures and intergranular current transport properties of bulk ex-situ MgB_2 fabricated using several heating durations to determine the key microstructural factors that influence the connectivity of the ex-situ fabricated MgB_2 superconductors. We determined that the in- and ex-situ MgB_2 exhibit remarkably different distributions, shapes, and pore sizes. Moreover, MgB_4 impurity phase is formed during long periods of sintering, decreasing the packing factor and connectivity in bulk ex-situ MgB_2 . Finally, we propose guidelines for the microstructural optimization of the ex-situ method.

2. Experimental

2.1 Preparation of bulk samples

Bulk ex-situ MgB₂ was fabricated from laboratory-made MgB₂ powder, which was prepared by the powder in the closed-tube method [26] (heating condition: 900 °C for 2 h) synthesized from the mixed powders of Mg (99.5% purity) and B (99% purity) with a 1:2 molar ratio. Grinding was performed by milling in an agate mortar. The laboratory-made MgB₂ powder was placed in a stainless-steel (SUS316) tube that was then uniaxially compressed under 500 MPa with both the ends closed. The tube was then heated in an evacuated quartz ampoule. The sintering periods used for the bulk ex-situ MgB₂ preparation at 900 °C were systematically changed (i.e., 0, 24, 48, and 96 h). The sintered samples are labeled according to their sintering periods, e.g., sample-ex24 indicates an ex-situ sample sintered at 900 °C for 24 h and sample-in48 refers to an in-situ sample fabricated using heat treatment at 900 °C for 48 h. The detailed sample preparation information has been reported previously [36].

2.2 Measurement of superconducting properties

Magnetization was measured at 20 K using a SQUID magnetometer (Quantum Design: MPMS-XL5s). The J_c values for bulk samples with typical dimensions $1 \times 1 \times 0.5 \text{ mm}^3$ were calculated from the widths of magnetization hysteresis loops based on the extended Bean model [37] according to $J_c = 20\Delta M/a(1 - a/3b)$, where ΔM is the magnetization hysteresis loop width and a and b are the dimensions of the rectangular sample. Transport measurements were performed by the conventional four-point probe method with 15 Hz AC using a physical property measurement system (Quantum Design: PPMS Model 6000). The normal state electrical connectivity (K) of the samples was estimated using the equation $K = \Delta\rho_g/\Delta\rho$, where $\Delta\rho_g = \rho_g(300 \text{ K}) - \rho_g(40 \text{ K}) \equiv 6.32 \mu\Omega\cdot\text{cm}$ [13] and $\Delta\rho = \rho(300 \text{ K}) - \rho(40 \text{ K})$, which are the differences in the resistivities of ideal MgB₂ grains and those of an examined sample, respectively.

Sample mass densities were calculated by a micrometer caliper and weighing machine. The packing factor P was determined by dividing the measured bulk density by the theoretical MgB₂ density ($2.62 \text{ g}\cdot\text{cm}^{-3}$).

2.3 Microstructural observations

The microstructures of bulk MgB_2 samples were observed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM). The SEM samples were fabricated by wet mechanical polishing using ethanol and diamond particles with sizes 3.0, 1.0, and 0.3 μm that were then followed by chemical mechanical polishing using colloidal silica with a size of 30 nm. SEM observations were conducted using a Carl Zeiss ULTRA 55 equipped with a backscatter electron (BSE) detector that was operated at an accelerating voltage of 12 kV and a working distance of 3.0 mm. The BSEs form channeling contrast, which depends on crystal orientation. The grain sizes of MgB_2 were obtained by the electron backscatter diffraction (EBSD) technique operated at an accelerating voltage of 12 kV, a working distance of 15.0 mm, and a step size of 70 nm. In the EBSD technique, crystal orientations at the areas of electron beam illumination were obtained using an inverse pole figure (IPF) map. In this experiment, we defined a grain to be an area composed of more than five adjacent EBSD acquisition points with the same crystallographic orientation. An elemental distribution was obtained by energy-dispersive X-ray spectroscopy (EDS). The detected characteristic X-rays were B-K α (0.183 keV), O-K α (0.525 keV), and Mg-K α (1.253 keV).

The TEM samples were fabricated by a microsampling method using a focused ion beam mill (Hitachi High Technologies: FB-2000K, acceleration voltage: 30 kV). Samples were $20 \times 15 \mu\text{m}^2$ in area with thicknesses of less than 100 nm. We used a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with conventional TEM observations (FEI TECNAI-F20, acceleration voltage: 200 kV). The convergence semi-angle of the incident electron was 6 mrad, and the angular detection range of scattering electrons was 70–350 mrad.

3. Results

3.1 Packing factor, connectivity, and critical current density

Figure 1 shows the magnetic field dependence of J_c at 20 K for sample-ex0, sample-ex24, sample-ex48, and sample-ex96. J_c values were significantly higher after the initial 24 h sintering stage and continued to rise with increased sintering time.

Figure 2 shows the effects of sintering time on connectivity K and packing factor P for each sample. Both the connectivity and packing factor are enhanced with increased sintering time. However, the increase rate of packing factor in sintering for more than 48 hour is low because of the formation of coarse MgB_4 grains and fine MgO particles.

3.2 Microstructure

Before sintering, the SEM–BSE images of sample-ex0 presented in Figure 3 show many aggregates with sizes ranging from 2 to 20 μm . The aggregates are polycrystalline because the image contrast that depends on crystal orientations appears in the aggregates, as shown in Fig. 3(b). However, the aggregates do not connect with each other, as shown by the white arrowheads in Fig. 3(b). In addition, MgB_2 grains in an aggregate do not necessarily connect with each other, as shown by the arrowheads in Fig. 3(c). This was caused by the milling used in the preparation of the laboratory-made MgB_2 powder.

Figure 4 shows the SEM–BSE images of sample-ex24 after sintering. The low magnification image in Fig. 4(a) shows that the pores between the aggregates shrunk with sintering. However, large pores with a size of 20 μm still remained. The remaining pores are narrowly shaped in contrast to those of the large pores in in-situ MgB_2 . Sintering also results in some aggregates initiating connections with other aggregates, as shown by the white circles in Fig. 4(b).

Figure 5 shows the SEM–BSE images of sample-ex48. The low magnification image in Fig. 5(a) shows that the areal density of large plate-like pores between the MgB_2 grain aggregates is less than that in sample-ex24. This indicates that self-sintering improved connections between the aggregates in addition

to improving macroscopic densification. In addition, the fine pores between MgB_2 grains in the aggregates mostly shrunk compared to those of sample-ex0 before sintering (Fig. 3(c)). Figure 6 shows the SEM–BSE images of sample-in48 fabricated in the same conditions as sample-ex48. The low magnification image in Fig. 6(a) shows two types of pores. First, large pores with sizes in the range of several tens of micrometers were formed by the melting of Mg powder. These pores are the main reason for the low packing factor of the in-situ MgB_2 [13]. In addition, small pores with a size of approximately $2\text{ }\mu\text{m}$ form in MgB_2 regions; these small pores appear more clearly in the high magnification image (Fig. 6(b)) of an MgB_2 region at the points indicated by the white arrowheads. Conversely, no plate-like pores were present in the ex-situ MgB_2 . The bright particles shown by the broken arrows in Fig. 6(b) are MgO particles.

Figures 7(a) and (b) show the SEM–BSE images of sample-ex96. The pores between the polycrystalline MgB_2 aggregates shrunk, and connections between the aggregates improved in comparison to sample-ex48 in Fig. 5(a). As shown in Fig. 7(b), three types of regions with different image intensities are present. The EDS elemental maps (Figs. 7(c)–(d)) indicate that the dark region (i) in Fig. 7(b) is enriched with boron (B-rich region), the medium brightness region (ii) is the MgB_2 -forming region, and the bright region (iii) is enriched with oxygen (O-rich region). Figure 8 shows (a) the HAADF-STEM image and SEM–EDS (b)–(d) elemental maps acquired from the square area shown in Fig. 8(a). Figures 8(e) and (f) are electron diffraction patterns acquired from the O- and B-rich regions shown by the solid circles in Fig. 8(a). The diffraction patterns indicate that the O-rich region consists of MgO, and the B-rich region consists of MgB_4 . Some MgO particles form MgO aggregates between the MgB_2 aggregates, as indicated by the broken circles in Fig. 8(a). These MgO particle aggregates may interfere with connections between the MgB_2 aggregates. Connected areas between MgB_2 aggregates without MgO particles are expected to act as transport current paths; however, their width is rather narrow and is approximately 500 nm , as indicated by the solid arrowhead in Fig. 8(a).

Figure 9 shows the SEM–EBSD crystal orientation maps and average grain sizes of MgB_2 for (a) sample-ex0, (b) sample-ex24, (c) sample-ex48, and (d) sample-ex96. The color variation indicates crystal orientations, as shown by the stereo-triangle color key in Fig. 9(e). In the black regions, EBSD patterns could not be obtained because of the existence of pores, secondary phases, and grain boundaries. The average grain size of the ex-situ samples is approximately 400 nm. This indicates that no grain growth of MgB_2 occurred during sintering. Figure 9(f) shows the distribution of angles between the direction perpendicular to the sample surface and the $[0001]$ or $[1\bar{1}20]$ axes of sample-ex96 calculated by the IPF maps. The sample does not exhibit strong texture, and the crystal orientation shows random distribution, as in the case of sample-in48 (Fig. 10). Figure 10 shows the IPF maps of (a) the MgB_2 -formed region and (b) a region near a large pore formed by the melting of Mg for the sample-in48. The average MgB_2 grain size is approximately 380 nm in Figs. 10(a) and (b), and MgB_2 grain sizes distributions follow the same trend. This shows that MgB_2 grain sizes are uniform over the entire region of sample-in48. Figure 10(c) shows the distribution of the angle between the direction perpendicular to the sample surface and the $[0001]$ or $[1\bar{1}20]$ axes calculated by the IPF maps. The distribution shows no texture, the distribution of MgB_2 crystal orientations in sample-in48 is random.

4. Discussion

We first discuss the microstructural evolution of ex-situ MgB_2 during sintering. As shown in Fig. 3, two types of pores observed in the bulk ex-situ MgB_2 precursor (sample-ex0) become smaller as the precursor is sintered. This is accompanied by the aggregates of MgB_2 grains starting to connect with each other in the initial stage of sintering, as shown in sample-ex24 (Fig. 4). This is the reason for the remarkable improvement in connectivity during the initial stage of sintering. At the mid-stage of sintering shown by sample-ex48 (Fig. 5), connections between MgB_2 grain aggregates are better than those in sample-ex24; this may possibly be the cause for the continuous rise in the connectivity and J_c value with increased

sintering time. However, connectivity increases at a smaller rate than in the initial stages of sintering. This may be due to the MgO particle aggregates interrupting the connections between the MgB₂ grain aggregates, as shown in Fig. 8. The examination of sample-ex96 shows that at the later stage of sintering, connections between MgB₂ grain aggregates are further improved, as shown in Fig. 7. However, MgB₄ grains and MgO particle aggregates are also present. These impurity phase areas are formed due to the decomposition of MgB₂ during sintering at high temperature (i.e., 900 °C) and over a long time (i.e., 96 h). MgB₂ grain sizes show almost no change during sintering. This suggests that the dispersed MgO particles may pin MgB₂ grain boundary migration, and consequently, MgB₂ grains did not show grain growth.

We now compare the microstructures of in- and ex-situ MgB₂ fabricated at the same sintering condition. Figure 11 shows schematic diagrams that illustrate the differences between the two microstructures. MgB₂ grain sizes and orientation distributions are almost the same in all the samples regardless of the sintering time. This indicates that MgB₂ phase formation is almost completed when sample-ex0 (precursor) was pre-reacted at 900 °C. It also shows that MgB₂ grains grow slowly during the further sintering at 900 °C. While two types of pores are present for both bulk in- and ex-situ MgB₂, the pore characteristics are different. In the in-situ MgB₂, large pores are formed by the penetration of Mg; these pores decrease the current path, increase the current percolation length, and largely reduce the macroscopic connectivity. Small pores that are approximately less than 1 μm are also present and remain on the MgB₂ grain boundaries during sintering. These small pores slightly degrade the intergranular connectivity and current paths in bulk in-situ MgB₂. In contrast, for the case of bulk ex-situ MgB₂, the connectivity and current paths are limited by large pores greater than 10 μm distributed between MgB₂ grain aggregates. In bulk ex-situ MgB₂, the current path is narrow because the connected area between MgB₂ grain aggregates is narrow due to the presence of pores and MgO particles between the aggregates. This appears to be the reason for the bulk ex-situ MgB₂ exhibiting a low connectivity regardless of a high

packing factor.

Based on the findings of the present study, we consider guidelines for enhancing the MgB_2 grain connectivity in bulk ex-situ MgB_2 . To enhance the connectivity, the connected area between MgB_2 grain aggregates should be increased. Note that the loaded tension on the pores in a sintered compact becomes stronger as the pore size is reduced. Therefore, the pore size reduction before sintering would lead to better connections between MgB_2 grain aggregates. In other words, a high packing factor should first be achieved by reducing the size of MgB_2 grain aggregates. The presence of MgO particles between the MgB_2 grain aggregates also degrades the connectivity of the MgB_2 grain aggregates. Conversely, MgO particles tend to disperse uniformly in bulk in-situ MgB_2 and can be expected to improve flux pinning and control grain growth by pinning grain boundary migration in bulk in-situ MgB_2 . However, for the case of bulk ex-situ MgB_2 , MgO particles do not uniformly disperse but rather form their own aggregates between the MgB_2 grain aggregates. Such nonuniform dispersions of MgO particles may occur by the movement of MgO particles on the surface of MgB_2 grain aggregates during sintering. To avoid the aggregation of MgO particles on the surface of MgB_2 grain aggregates, MgO should be removed from the surface of initial MgB_2 powders before sintering by a mechanical process such as ball milling. Furthermore, the movement of MgO should be suppressed in ex-situ MgB_2 by shortening the sintering time.

5. Conclusions

In this study, we elucidated the microstructures of bulk ex-situ MgB_2 to develop a strategy for the further enhancement of the connectivity and J_c of MgB_2 . The morphology of pores in bulk ex-situ MgB_2 differs from that in bulk in-situ MgB_2 . The large plate-like pores between MgB_2 grain aggregates reduce the connectivity and J_c in bulk ex-situ MgB_2 . In addition, MgO particles form their own aggregates between the MgB_2 grain aggregates; the presence of these MgO particle aggregates may possibly

interrupt connections and current paths between the MgB_2 grain aggregates. Unlike the case of ex-situ MgB_2 , the microstructure of the in-situ MgB_2 fabricated at the same sintering condition does not exhibit any plate-like pores and MgO particle aggregates. Therefore, a strategy for enhancing the connectivity in bulk ex-situ MgB_2 should focus on two issues: (a) the reduction of the pore sizes before sintering and (b) the inhibition of MgO particle formation and their aggregation.

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Figure captions

Fig. 1 Magnetic field dependence of critical current density J_c at 20 K for bulk ex-situ MgB_2 with different sintering period.

Fig. 2 Sintering effects on connectivity (left axis) and packing factor (right axis) for bulk ex-situ MgB_2 .

Fig. 3 SEM–BSE image of sample-ex0 ($K = 0.15\%$). (a) Low and (b), (c) high magnification images. White arrows in (a) indicate aggregates that consist of MgB_2 grains. These MgB_2 grains are identified by broken arrows in (b). Sample-ex0 contains two types of pores: pores existing between the aggregates, as shown by white arrowheads in (b), and fine pores existing between MgB_2 grains, as indicated by broken arrows in (c). The analyzed connectivity and packing factor are given at top right and bottom left in (a), respectively.

Fig. 4 SEM–BSE image of sample-ex24 ($K = 13\%$). (a) Low and (b) high magnification images. A white arrow in (a) indicates remaining large pores between aggregates. The aggregates contact each other, as indicated by the circles in (b). The analyzed connectivity and packing factor are given at top right and bottom left in (a), respectively.

Fig. 5 SEM–BSE image of sample-ex48 ($K = 18\%$). (a) Low and (b) high magnification images of an aggregate. The large pores in sample-ex48 are smaller than those in sample-ex24, and those between MgB_2 grains are almost eliminated. The analyzed connectivity and packing factor are given at top right and bottom left in (a), respectively.

Fig. 6 SEM–BSE observation results. (a) A low magnification image of sample-in48 and (b) a high magnification image of the MgB_2 crystallized area. White arrows in (b) show small pores. Broken arrows in (b) show MgO particles. The analyzed connectivity and packing factor are given at top right and bottom left in (a), respectively.

Fig. 7 SEM–BSE images and EDS electron maps of sample-ex96 ($K = 21\%$). (a) A low magnification image of sample-ex96 ($K = 21\%$). Dark regions are rich in boron, and bright regions are rich in oxygen. B- and O-rich areas in (a) were identified by comparison with (b) an SEM–BSE image the EDS elemental maps for (c) Mg, (d) B, and (e) O acquired from the area (b). The analyzed connectivity and packing factor are given at top right and bottom left in (a), respectively.

Fig. 8 (a) HAADF-STEM image of sample-ex96. (b)–(d) STEM–EDS elemental maps for (b) Mg, (c) B, and (d) O acquired from the square area denoted in (a). (e), (f) Electron diffraction patterns taken from the encircled areas in (a). Bright areas in (a), which are denoted by broken circles, correspond to O-rich areas and consist of MgO particles. The B-rich crystal, which is indicated by the white broken arrow in (a), is a MgB_4 single crystal. White arrows show connection areas between MgB_2 grain aggregates. The widths of the connected part are narrower than $1\ \mu\text{m}$.

Fig. 9 IPF maps of (a) sample-ex0, (b) sample-ex24, (c) sample-ex48, and (d) sample-ex96. (e) A color key for correspondence between grain orientations and colors variations on the IPF maps. The average MgB_2 grain size is given at the top right of each maps. Most MgB_2 grains are smaller than or equal to $2\ \mu\text{m}$. (f) Grain direction of sample-ex96 shows the angle between the direction perpendicular to the sample surface and axes $[0001]$ or $[1\ \bar{1}20]$.

Fig. 10 IPF maps of sample-in48. (a) The central part of an MgB₂ crystallized region and (b) near a large pore. The average MgB₂ grain size is denoted at the top right of each maps. (d) Grain direction shows the angle between the direction perpendicular to the sample surface and axes [0001] or [1 $\bar{1}$ 20].

Fig. 11 Schematic diagrams of microstructures in (a) in- and (b) ex-situ MgB₂ fabricated by sintering for 48 h at 900 °C. In-situ MgB₂ contains large pores that are caused by the penetration of Mg atom from Mg powder regions, although pore sizes contained in MgB₂ crystallized areas are approximately 2 μm. In contrast, ex-situ MgB₂ contains large pores between aggregates. Therefore, the boundary widths between MgB₂ grain aggregates are only at the submicrometer scale. Furthermore, some boundaries between MgB₂ grain aggregates contain MgO particles, which interfere with the connections between MgB₂ grain aggregates.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

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Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11