Towards the Realization of Higher Connectivity in MgB$_2$ Conductors: In-situ or Sintered Ex-situ?

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1. Introduction

One of the distinct characteristics of MgB$_2$ among the high-temperature superconductors (HTSs) is its conventional metallic superconductivity, i.e., s-wave symmetry of pairing, high carrier density, long and rather isotropic coherence length, together with the high critical temperature $T_c = 40$ K and high upper critical field $B_{c2} > 50$ T. These characteristics bring in a strongly linked current flow in randomly oriented polycrystalline and an easy fabrication of long length wires by the common power-in-tube (PIT) method. Additionally, they are simply a intermetallic line compound from two light elements, Mg and B, and an inexpensive material additionally, being a simple intermetallic line compound from two light elements, Mg and B, and an inexpensive material.

The two most common types of MgB$_2$ conductor fabrication technique—in-situ and ex-situ—show increasing conflicts concerning the connectivity, an effective current-carrying cross-sectional area. An in-situ reaction yields a strong intergrain coupling with a low packing factor, while an ex-situ process using pre-reacted MgB$_2$ yields tightly packed grains, however, their coupling is much weaker. We studied the normal-state resistivity and microstructure of ex-situ MgB$_2$ bulks synthesized with varied heating conditions under ambient pressure. The samples heated at moderately high temperatures of $\sim 900$°C for a long period showed an increased packing factor, a larger intergrain contact area and a significantly decreased resistivity, all of which indicate the solid-state self-sintering of MgB$_2$. Consequently the connectivity of the sintered ex-situ samples exceeded the typical connectivity range 5–15% of the in-situ samples. Our results show self-sintering develops the superior connectivity potential of ex-situ MgB$_2$, though its intergrain coupling is not yet fulfilled, to provide a strong possibility of twice or even much higher connectivity in optimally sintered ex-situ MgB$_2$ than in in-situ MgB$_2$. © 2012 The Japan Society of Applied Physics

The reported values of critical current density $J_c$ at 20 K for MgB$_2$ bulks, wires and tapes $10^5–10^6$ A cm$^{-2}$ turned out to be apparently lower than the deparing current density, $J_d$ (20 K) $\sim B_{c2}/\mu_0 \lambda \sim 10^8$ A cm$^{-2}$, where $B_{c2}$ is the thermodynamic critical field, $\mu_0$ is the permeability of vacuum and $\lambda$ is the penetration depth. Indeed very high $J_c$ values reaching $10^7$ A cm$^{-2}$ at 20 K have been reported for epitaxial thin films. Grain boundaries work as predominant flux pinning centers in MgB$_2$ and the doping of carbon-based compounds, such as graphite, B$_4$C, SiC, and organic compounds are reported to be effective in increasing $J_c$. The degradation of crystallinity, i.e., the distortion of honeycomb boron lattice, is believed to be the origin of the enhancement of flux pinning for both cases and particularly contributes to the improvement of $J_c$ under high magnetic fields.

A reduction in the effective current-carrying cross-sectional area of the sample was suggested by Rowell to explain the large gap of $J_c$ between films and wires. The Josephson junction model of the grain boundaries, the two-band model, and the oxide barrier model were considered to affect the limited transport properties of MgB$_2$. In our previous study, we applied a mean-field theory to the three-dimensional percolation problem to understand the anomaly suppressed connectivity in rather weak-link-free MgB$_2$ polycrystals. The mean-field theory quantitatively showed that the packing factor ($P$) of polycrystals, impurity layers at grain boundaries, and anisotropy are the limiting factors of the connectivity.

In-situ and ex-situ methods have been developed to manufacture MgB$_2$ bulks, wires, and tapes. Perhaps the most commonly studied method is the in-situ method, that is the formation of MgB$_2$ simply from mixed powders of Mg+2B, since a relatively high $J_c$ value is easily attained owing to its reasonably strong intergrain coupling. In an in-situ reaction process, Mg grains melt and diffuse into B grains, and transform into voids resulting in a low bulk density ($P \sim 50\%$) and a low connectivity. On the other hand, the ex-situ method using prereacted MgB$_2$ powder is favorable in terms of bulk density. A packing factor close to 75% (the close packing of spheres) can be expected. Even unsintered, as-pressed ex-situ MgB$_2$ tapes show a relatively high transport $J_c$ value of $\sim 10^4$ A cm$^{-2}$ at 20 K. Heat treatment after cold working is effective in improving $J_c$ through the strengthening of intergrain coupling. The $J_c$ of heat treated ex-situ MgB$_2$ is, however, generally lower than that of in-situ MgB$_2$, likely due to the fact that intergrain coupling is insufficient compared with the strong coupling in the in-situ MgB$_2$. The connectivity of reasonably high $J_c$ ex-situ MgB$_2$ tapes is reported to be less than 10%, which is obviously lower than the typical connectivity of in-situ MgB$_2$, 5–15%. Since the packing factor of ex-situ MgB$_2$ is higher than that of in-situ MgB$_2$, a better connectivity, even higher than that of in-situ, is naturally expected if a strong intergrain coupling is achieved.

In this paper we carefully investigated the microstructure, normal-state resistivity and electrical connectivity of ex-situ MgB$_2$ polycrystalline bulks prepared using systematically varied heating conditions under ambient pressure. In particular we employed long heat treatments at high temperatures of $\sim 900$°C to promote the self-sintering of MgB$_2$ grains. In order to prevent the decomposition of MgB$_2$ by the vaporization of Mg at high temperatures, prereacted MgB$_2$ powders were sealed and heated in a metal sheath using our...
Conducting transition is broad with the resistivity of the as-pressed bulk does start dropping at the temperature for the MgB$_2$ powder or commercially available MgB$_2$ powder (99% purity, several tens of microns in size, Alfa Aesar) was used as a starting material. The MgB$_2$ powder was filled into a stainless-steel (SUS316) tube, then the tube was uniaxially pressed under 500 MPa with both ends closed by mechanical pressing. Finally each tube was heated at 750–950°C for 3–96 h in an evacuated quartz ampoule. Laboratory-made MgB$_2$ powder was prepared by grinding the in-situ-processed bulk (heating condition: 900°C for 2 h) synthesized from mixed powders of Mg (99.5% purity) and B (99% purity) with the molar ratio of 1:2. In-situ- and diffusion-processed bulks were prepared from Mg and B powders for comparison.

Constituent phases of the samples were analyzed by the powders X-ray diffraction (XRD) method using Cu Kα radiation. Microstructural observation was performed using a scanning electron microscope (SEM; JEOL JSM-7000F). The packing factor (P) of the samples was measured using a micrometer caliper and a weighing balance. Resistivity measurements were performed by the conventional four-point probe method with an ac current of 15 Hz using a physical property measurement system (PPMS; Quantum Design PPMS Model 6000).

3. Results and Discussion

3.1 Resistivity and connectivity

Figure 1(a) shows the electrical resistivity $\rho$ as a function of temperature for the ex-situ bulks from laboratory-made MgB$_2$ powder with a systematically varied degree of sintering, by heating at different temperatures from 750 to 900°C. The as-pressed MgB$_2$ bulk before heat treatment, in-situ bulk, and diffusion bulk are also shown for comparison. The as-pressed bulk has a large resistivity of ~1 x 10$^5$ μΩ cm at room temperature and shows an unusual temperature dependence with a very slight upturn below ~100 K, resulting in low $RRR = \rho(300 \text{ K})/\rho(40 \text{ K}) = 1.1$. The resistivity of the as-pressed bulk does start dropping at ~39 K and reaches zero resistance; however, its superconducting transition is broad with $\Delta T_c > 10 \text{ K}$ [Fig. 1(b)]. The high $\rho$ and small $RRR$, and large $\Delta T_c$ suggest that intergrain coupling is weak. On the other hand, the ex-situ bulks heated at above 850°C show a successively lower resistivity as the heat treatment temperature increases, indicative of evolution of intergrain coupling by sintering. Indeed we observed an increase in packing factor for the heat-treated bulks compared to the as-pressed bulk. The bulk heated at 900°C for 48 h, with the highest degree of sintering, shows resistivities of 50 μΩ cm at 300 K and 15 μΩ cm at 40 K, which are 2 or 3 orders of magnitude lower than that of the as-pressed bulk and even lower than that of the typical in-situ bulk. Consequently the resistive transition becomes sharper with the progression of sintering, and the bulks sintered above 850°C show small $\Delta T_c < 1 \text{ K}$ which is comparable to that of the in-situ bulks.

The evolution of transport current connectivity by sintering is summarized in Fig. 2. The zero resistance temperature $T_{R0}$ is defined by $\rho < 10^{-6} \mu\Omega \text{ cm}$. The electrical connectivity $K = \Delta \rho_g/\Delta \rho$, where $\Delta \rho_g = \rho(300 \text{ K}) - \rho(40 \text{ K}) = 6.32 \mu\Omega \text{ cm}$ and $\Delta \rho = \rho(300 \text{ K}) - \rho(40 \text{ K})$ are the difference in resistivity of the ideal MgB$_2$ grains and that of a sample, respectively, is plotted as a function of sintering temperature. Both $T_{R0}$ and $K$ show a rapid increase above 850°C, and the maximum connectivity is obtained for the bulk sintered at 900°C. Sintering above 950°C reduces connectivity, probably due to the decomposition of MgB$_2$ as evidenced by B-rich impurity phases observed by compositional analyses (not shown here). The prolonged heat treatment further promoted sintering and improvement in connectivity. The bulk sintered at 900°C for 48 h shows $K > 18\%$ which is among the highest values for MgB$_2$ polycrystals except samples synthesized by diffusion process or under high pressure. Here the connectivity of...
the sintered ex-situ bulks exceeds the typical range of in-situ processed bulks and wires which is 5–15%.

3.2 Microstructure

Figure 3 summarizes typical microstructural features of MgB$_2$ polycrystalline bulks prepared by in-situ [Fig. 3(a)] and ex-situ [Fig. 3(b)] methods. Here, gray, black, and white contrasts in the secondary electron images correspond to MgB$_2$ grains, pores, and impurity phases, such as MgO, respectively. The in-situ-processed sample shows a porous microstructure with large voids typically 10–50 μm in size. Spaces filled with Mg powders before the heat treatment transform into voids through the reaction with B. On the other hand, a characteristic microstructure different from that of the in-situ bulk can be seen in the ex-situ bulk sintered at 900 °C for 24 h. In Fig. 3(b) islands of MgB$_2$ grains and particles with a size of ~10 μm are dispersed and the voids occupy the gap between the islands. For the ex-situ bulk, the shape of the voids is apparently different from that of the in-situ bulk, and their size is much smaller (typically less than 10 μm). One can see that the intergrain coupling between MgB$_2$ grains/particles is poor in contrast to that in the in-situ sample where a strongly linked network of MgB$_2$ grains is observed. The weak intergrain coupling is considered to be the reason for the rather restricted $K$ observed in the ex-situ bulk [Fig. 1(a)] though the packing factor of the ex-situ bulk (64%) is much higher than that of the in-situ bulk (48%).

Higher magnification images of the polished cross-sectional surface of MgB$_2$ bulks are shown in Fig. 4 to manifest intergrain coupling between MgB$_2$ grains. The as-pressed MgB$_2$ bulk before sintering shows fine MgB$_2$ grains/particles are tightly packed and neither of intergrain or grain-particle coupling can be seen [Fig. 4(b)]. After
heating at 900 °C, the surface area of MgB_2 grains decreased and the size of voids increased compared with those observed in the as-pressed and coupling between MgB_2 grains/particles were also clearly observed [Fig. 4(c)], all of these suggest that solid-state self-sintering occurred during the heat treatment. On this magnification scale, we did not observe impurity phases or cracks at grain boundaries of the sintered ex-situ MgB_2 bulk. Though the area of coupling between grains in the sintered ex-situ bulk is smaller than that in the in-situ bulk [Fig. 4(a)] such coupling is believed to contribute significantly as an effective path for the transport current in both normal and superconducting states.

4. Discussion

It is well known that the J_c of the ex-situ MgB_2 can be largely enhanced by heat treatment. The improvement of intergrain coupling by sintering or the removal of volatile impurities from grain boundaries can be considered as the reason. However, there are few reports on the self-sintering of MgB_2. Danceur et al. studied the effects of a range of heat treatment (widely varied from 200 to 1100 °C for 1 h) on the packing factor and the amount of the MgO impurity phase for ex-situ MgB_2 bulks. After heat treatments they observed little sign of sintering even at 1100 °C and a small change (<3%) in packing factor. Our bulk samples showed a partially sintered microstructure which is similar to that of spark-plasma-sintered (SPS) or high-pressure-processed bulks together with an approximately 10% increase in packing factor. The lowered resistivity by the heat treatment (widely varied from 200 to 1100 °C) results in twice or three times higher connectivity in the ex-situ bulks, the result indicates that either critical packing factor P_c is higher and/or intergrain coupling between MgB_2 grains/particles (which corresponds to a) is weaker in the sintered ex-situ bulks. Considering that the contacted area between MgB_2 grains in the ex-situ bulks is limited by the porosity gaps [Figs. 3(b), 4(c)], it is considered that intergrain coupling is still insufficient compared with that in the in-situ bulks.

Thus far the connectivity of ex-situ MgB_2 is a trade-off balance between the higher packing factor and the weaker intergrain coupling. Equation (2) predicts a high connectivity of 30–40% for moderately sintered ex-situ MgB_2 with P ~ 75% owing to its large P_c. Just a ~25% increase in P compared with that in in-situ MgB_2 results in twice or three times higher connectivity in ex-situ MgB_2, if a sufficient arrangement of surface contact between grains is achieved. Our results suggest that under controlled atmosphere of Mg pressure, the solid-state self-sintering of MgB_2 occurs and significantly improves the intergrain coupling by heat treatment under an ambient pressure. Given that homogeneous, single starting powder is favorable for the fabrication of wires by the PIT method, sintered ex-situ MgB_2 has advantages in both connectivity and long-length wire fabrication. We believe the issues on the microstructure of sintered ex-situ MgB_2 bulks, such as large agglomerates and gaps between grains, can reasonably be solved by the
optimization of powder preparation and heat treatment conditions in near future.

Finally we briefly mention the $J_c$ of sintered ex-situ MgB$_2$. What surprised us is that the long heat treatment did not yield a significant increase in grain size. Indeed the sintering promoted agglomerate formation; however, it just enhanced surface contact and did not promote grain growth [Fig. 4(c)]. This is in strong contrast to that observed in in-situ MgB$_2$ bulks heated at high temperatures for a long period where grain growth occurred and a marked deterioration in $J_c$ was observed. We observed a higher $J_c$ value in the sintered ex-situ bulks than in the optimized in-situ bulks. Such critical current properties in the relationship between the connectivity and microstructure of the sintered ex-situ bulks will be reported in detail in a subsequent paper. 33)

5. Conclusions

We studied the normal-state resistivity and microstructure of ex-situ MgB$_2$ bulks synthesized with varied heating conditions under ambient pressure. The samples heated at moderately high temperatures of $\sim$900 °C for a long period showed an increased packing factor, a larger intergrain contact area, and a significantly decreased resistivity, all of which indicate the solid-state self-sintering of MgB$_2$. Consequently the connectivity of the sintered ex-situ samples exceeded the typical connectivity range 5–15% of the in-situ samples. Our results show self-sintering can develop the superior connectivity potential of ex-situ MgB$_2$, though its intergrain coupling is not yet fulfilled, to provide a strong possibility of realizing twice or even much higher connectivity in optimally sintered ex-situ MgB$_2$ than in in-situ MgB$_2$.

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