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High-performance dense MgB₂ superconducting wire fabricated from mechanically milled powder

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Abstract
Owing to the relatively high critical temperature and the low manufacturing cost, MgB₂ superconducting wires are promising for liquid helium-free superconducting applications. Today, commercially available MgB₂ wires are manufactured by either an in situ or ex situ powder-in-tube process, the in situ process being more effective to obtain high critical current density. In in situ-processed wires, however, the critical current density is seriously suppressed by the high porosity of MgB₂ filaments. To resolve this problem, we propose an innovative method of using precursor powder prepared by mechanical milling of magnesium, boron, and coronene powders. This precursor powder has a metal–matrix–composite structure, in which boron particles are dispersed in a magnesium matrix. The plastic deformation of the precursor powder through wire processing leads to compact packing, and a dense MgB₂ filament is generated after heat treatment. As a result, the limitation of critical current density that occurs for the typical in situ process is overcome, and the practical critical current density of 10³ A mm⁻² is obtained at 10 K and 6.1 T, at 15 K and 4.8 T, and at 20 K and 3.3 T.

Keywords: MgB₂, superconducting wire, mechanical milling, critical current density, connectivity, liquid helium-free

(Some figures may appear in colour only in the online journal)

1. Introduction
Owing to the relatively high critical temperature \( T_c \approx 40 \text{ K} \) and the low manufacturing cost, since its discovery in 2001 [1], magnesium diboride (MgB₂) has been recognized as a promising material for liquid helium-free superconducting applications operating at 10–20 K by conduction cooling or in liquid hydrogen, such as MRI scanners [2, 3], transmission cables [4], wind turbines [5], energy storage [6], and aircraft components [7]. In MgB₂, macroscopically uniform supercurrent flows without any crystalline orientation [8] because of the lack of weak-link behaviour at grain boundaries [9]. This feature enables practical MgB₂ wires to be manufactured by the powder-in-tube (PIT) process, in which a metallic billet filled with powder is processed into a thin wire. Today, PIT-processed MgB₂ wires have been supplied on a commercial basis [10, 11].
Processes for manufacturing the commercially available PIT-processed MgB$_2$ wires are classified as either in situ [10] or ex situ [11]. The in situ process is based on ‘chemical synthesis’: a mixture of magnesium and boron powders is converted into MgB$_2$ by heat treatment after wire processing. The ex situ process is based on ‘self-sintering’: MgB$_2$ powder is sintered after processing into a wire. Despite various refinements of MgB$_2$ powder for the ex situ process [12, 13], as of now, the in situ-processed wires have a superior critical current density, $J_c$, compared to the ex situ-processed wires because the self-sintering of MgB$_2$ particles is extremely difficult. Nevertheless, the in situ process has room for improvement.

A major problem for the in situ process is the high porosity of MgB$_2$ filaments. In the PIT-processed wires, the packing factor of MgB$_2$, $P$, is given by

$$P = P_i(1 - \Delta \nu),$$

(1)

where $P_i$ and $\Delta \nu$ are the packing factor of the precursor powder after wire processing and the ratio of volume reduction in a chemical reaction, respectively. Owing to the difficulty in packing powder particles compactly, in general, $P_i$ has a smaller value than 1. For the in situ process, in addition, the volume of a filament is reduced by $\Delta \nu \cong 0.25$ [14] because the real densities of magnesium and boron are lower than that of MgB$_2$. Consequently, MgB$_2$ filaments synthesized by the in situ process are porous, and the low packing factor of MgB$_2$ suppresses $J_c$ [15]. To overcome the limitation of $J_c$ that occurs in the conventional processes, new routes, such as internal magnesium diffusion [16–18] and mechanical milling/alloying [19–21], and high pressure treatments, such as cold high pressure densification [22] and hot isostatic pressing [23], have been developed.

Here, we focus on mechanical milling. This differs from the typical in situ process in the way magnesium and boron powders are mixed. In the case of the typical in situ process, the powder is mixed gently; in the case of mechanical milling, the powder is crushed with balls by a planetary mill. In previous studies, mechanical milling was mainly used to improve the reactivity of precursor powder [21] or to synthesize nano-crystalline MgB$_2$ by mechanochemical reaction [19, 20]. In the latter case, in particular, the powder processing is called mechanical alloying.

In this study, we use mechanical milling as a way to reduce the porosity of MgB$_2$ filaments concerning the typical in situ process. Figure 1 illustrates the scheme to improve the packing factor. In the case of the typical in situ process, whereas soft magnesium particles are deformed through wire processing [24], hard boron particles are not deformed. As a result, spaces are left among the boron particles ($P_i < 1$). During heat treatment, magnesium atoms move toward the boron particles, and elongated voids are generated. In the case of our approach, metal–matrix–composite particles, in which boron particles are dispersed in a magnesium matrix, are formed by mechanical milling. If the precursor particles are deformed through wire processing, compact packing is achieved ($P_i \cong 1$). By inserting $P_i \cong 1$ and $\Delta \nu \cong 0.25$ into equation (1), the expected MgB$_2$ packing factor is estimated to be $P \cong 0.75$. This packing factor is about 0.15 higher than that of typical in situ-processed wires, $P \cong 0.6$ [25]. To confirm the proposed scheme, a wire fabricated from mechanically milled powder is compared with several typical in situ-processed wires in terms of microstructure and electromagnetic properties.

2. Methods

Table 1 lists the specifications of the MgB$_2$ superconducting wires of which properties are compared in this study. Wire-MMC and wire-INC were newly fabricated in this study. Wire-IN [25] and wire-INC-10 [26] are reported in our previous study. Wire-INC-HT is a standard wire that is supplied by Hyper Tech Research Inc., and its $J_c$ is reported in [27]. For wire-MMC and wire-INC, used as starting materials, magnesium (>99.8%), boron (>98.5%, <250 nm; Pavezyum nano Boron), and coronene (>83.0%) were mixed at a molar ratio of Mg: B: C$_{24}$H$_{12}$ = 1: 2(1 – x): x/12, where $x$...
corresponds to the ratio of carbon to the total amount of boron and carbon. For wire-MMC, magnesium powder smaller than 200 mesh was used, and the starting materials were mixed at \( x = 0.02 \) by a planetary mill with zirconia tools with a revolution diameter of 70 mm at a revolution speed of 400 mm min\(^{-1}\) for 6 h with a ball-to-powder mass ratio of 13.5. For wire-INC, magnesium powder smaller than 325 mesh was used, and the starting materials were mixed gently at \( x = 0.03 \) by a pot mill. The mixtures were pelletized and packed into pure iron pipes with inside and outside diameters of 13.5 and 18.0 mm, respectively. The mixing, pelletizing, and packing of the powder were conducted in an argon atmosphere. The pipes were processed into wires 0.5 mm in diameter. The wires were heat-treated in an argon atmosphere to generate MgB\(_2\).

Transport \( J_c \) was measured by the four-probe method at a criterion of 1 \( \mu \text{V cm}^{-1} \). Cylindrical MgB\(_2\) filaments, which were about 0.3 mm in diameter and about 10 mm in length, were extracted by removing the outer iron sheath. Magnetization of the filaments was measured by a SQUID magnetometer (Quantum Design: MPMS) and magnetic \( J_c \) was calculated by using the extended Bean model for cylindrical superconductors in perpendicular magnetic fields, given as

\[
J_c = \frac{3\pi}{4} \frac{M}{d},
\]

where \( d \) is the diameter of the filaments and \( M \) is the width of the magnetization hysteresis loop. Resistivity of the filaments was measured by the four-probe method with an excitation current of 10 mA at 16 Hz (Quantum Design: PPMS). Perpendicular magnetic fields were applied to the samples for the measurements of the transport \( J_c \), magnetization, and resistivity. The density of the MgB\(_2\) filaments was calculated from the weight, length, and diameter. Constituent phases and lattice constants were evaluated from powder x-ray diffraction using Cu-K\(_{\alpha}\) radiation (Rigaku: RINT2500HL). Longitudinal cross-sections of the wires, which were prepared by dry polishing and argon-ion polishing, were observed by a scanning electron microscope (JEOL: JSM-7001F).

### 3. Results and discussion

Figure 2 shows the longitudinal cross-sections of wire-INC-10 and wire-MMC. These microstructures are consistent with the scheme illustrated in figure 1. In wire-INC-10 after wire processing, magnesium particles are elongated to several micrometers in diameter and spaces remain among the nanosized boron particles (figures 2(a) and (b)). In wire-INC-10 after heat treatment, MgB\(_2\) filaments contain a lot of elongated voids (figures 2(c) and (d)). In wire-MMC after wire processing, metal–matrix–composite particles of 10–100 \( \mu \text{m} \) are deformed longitudinally and packed compactly (figures 2(e) and (f)). After heat treatment, a dense MgB\(_2\) is generated (figures 2(g) and (h)). Figure 3 shows the powder x-ray diffraction profiles. For the precursor powder used for wire-MMC, all the peaks correspond to magnesium (figure 3(a)); hence, our powder processing is classified as not mechanical alloying but mechanical milling, and contamination from the milling tools is negligible. As a result, wire-MMC contains only a small amount of MgO as an impurity phase (figure 3(b)).

Figure 4 demonstrates the excellent performance of wire-MMC. Figure 4(a) shows the dependence of transport \( J_c \) on magnetic fields, \( B \), for the carbon-added wires. State-of-the-art preparation techniques are applied to the typical in situ processed wires. For wire-INC, as an example, fine boron powder was used, the heat treatment temperature was relatively low (600 °C), and an appropriate amount of coronene was added. It is well known that these preparation conditions effectively improve \( J_c \) [25, 28, 29]. Thus, wire-INC, wire-INC-10, and wire-INC-HT have sufficiently high \( J_c \) as in situ processed wires. Nevertheless, wire-MMC has a superior \( J_c \) to these wires. Figure 4(b) shows the dependence of magnetic \( J_c \) on \( B \) for the mono-filamentary wires. In many cases, carbon addition improves \( J_c \) at high magnetic fields but suppresses \( J_c \) at low magnetic fields [30, 31]. The behavior of magnetic \( J_c \) for wire-IN and wire-INC is consistent with this general tendency. In contrast, wire-MMC has a higher \( J_c \) than both wire-IN and wire-INC in a wide magnetic field range.

The increase in \( J_c \) by mechanical milling effectively broadens the utility of MgB\(_2\) wires. In general, most superconducting applications require a \( J_c \) of about 10\(^3\) A mm\(^{-2}\) [32]. In the case of MRI magnets, because 300 A mm\(^{-2}\) is required as an engineering \( J_c \) [27], 10\(^3\) A mm\(^{-2}\) is reasonable as a \( J_c \) target (considering that the ratio of the MgB\(_2\) area to the overall cross section is 10%–30% for practical multifilamentary wires [2, 10, 26]). Given that maximum acceptable magnetic field, \( B_{\alpha} \), is defined as a magnetic field where a \( J_c-B \) curve crosses the line at \( J_c = 10^3 \) A mm\(^{-2}\), wire-MMC...
has higher $B_a$ than the other typical in situ-processed wires. As an example, the applicable magnetic fields at 10, 15, and 20 K are as follows: 6.1, 4.8, and 3.3 T for wire-MMC; and 5.4, 4.2, and 2.8 T for wire-INC, respectively. Thus, mechanical milling enables MgB$_2$ wires to be utilized at higher magnetic fields or at higher temperatures.

To confirm the mechanism of the increase in $J_c$ by mechanical milling, lattice constants, packing factors, and electromagnetic properties are compared in Table 2. The packing factor, $P$, was defined as the ratio of the density of MgB$_2$ filaments to the real density of MgB$_2$, i.e., 2.63 g cm$^{-3}$.

Electrical connectivity, $K$, which corresponds to the ratio of the effective cross-sectional area for current flow, was estimated from the definition by Rowell [33]:

$$K = \frac{\Delta \rho G}{\Delta \rho}$$

where $\Delta \rho$ ($\equiv \rho(300 \text{ K}) - \rho(40 \text{ K})$) is the phonon term in the resistivity of MgB$_2$ filaments, and $\Delta \rho G$ (= 6.32 $\mu\Omega \text{ cm}$ [15]) is the corresponding value for ideal polycrystalline MgB$_2$ containing no voids or impurity phases. Intrinsic residual resistivity, $\rho_0$, which corresponds to the residual resistivity of a MgB$_2$ phase, was estimated from the formula by Matsushita et al [34]:

$$\rho_0 = K \times \rho(40 \text{ K})$$

To estimate critical temperatures, $T_c$, and upper critical fields, $B_{c2}$, 90% resistive transition was set as a criterion. Note that the estimation of $K$ and $\rho_0$ was not possible for wire-INC because a residual magnesium phase (see figure 3(d)) interfered with the evaluation of accurate $\Delta \rho$.

The high $J_c$ of the coronene-added wires at high magnetic fields is mainly caused by the increase in the upper critical field. Carbon atoms in coronene are substituted into boron sites in MgB$_2$. The actual carbon substitution ratios, $x_A$ in Mg$_{B_1-x_A}C_{x_A}$, which are estimated from the $a$ lattice constant as $x_A \cong 23.8 \times (0.3087 - a)$ [35], are 0.014 and 0.021 for wire-MMC and wire-INC, respectively. These moderate
carbon substitutions increase the electron scattering (ρ) without excessive suppression of $T_c$; consequently, Ginzburg–Landau coherence length is shortened, and $B_{c2}$ increases [36]. In fact, wire-MMC has twice as high $\rho$ as wire-IN, and wire-MMC and wire-INC has higher $B_{c2}$ than wire-IN by 1.5 T and 3.1 T, respectively. Meanwhile, the suppression of $J_c$ of wire-INC at low magnetic fields is due to the increase in the amount of the residual magnesium phase, which blocks supercurrent and should reduce $K$. The decrease in $K$ for carbon-added samples has been reported in several previous studies [30, 31].

The excellent $J_c$ of wire-MMC in a wide magnetic field range is mainly caused by the high packing factor and the high electrical connectivity. Mechanical milling enables spaces among boron particles to be filled with magnesium, and this filling leads to the increase in $P$ and $K$. In fact, wire-MMC has higher $P$ than wire-IN and wire-INC by 0.22 and 0.19, respectively, and wire-MMC has 1.6 times as high $K$ as wire-IN. Furthermore, a uniform reaction contributes to the excellent $J_c$ of wire-MMC. Though the coronene addition increases the amount of the residual magnesium phase in the case of the typical in situ process, wire-MMC contains a negligible amount of the residual magnesium phase (figure 3). For wire-MMC, the homogeneous distribution of magnesium and boron in the metal–matrix–composite powder causes the uniform reaction.

Here, the obtained values of the packing factor and electrical connectivity are discussed in more detail. For wire-MMC, the obtained packing factor, $P = 0.82$, is somewhat higher than the expected one, $P \approx 0.75$. This discrepancy may be due to the dimensionality reduction in the course of self-sintering following chemical synthesis. The expected packing factor was estimated from equation (1) on the assumption that the dimensions of the filament are not changed during heat treatment; thus, if the dimensions of the filament are reduced, it is possible for the actual packing factor to exceed the expected one. The dimensionality reduction is reported for ex situ-processed bulks heat-treated at 900 °C [37]. The estimation of $K$ for wire-MMC has somewhat less accuracy because $\rho K$ depends on the carbon substitution ratio in MgB$_2$. However, because the $K$ of wire-MMC seems to be underestimated, the argument that wire-MMC has higher $K$ than wire-IN is correct. By using the data of Wilke et al [38], Senkowicz et al [39] concluded that $\rho K$ is an increasing function of the carbon substitution ratio in MgB$_2$. Because a constant value was used as $\Delta \rho K$ for estimating $K$ in this study, the estimated $K$ for wire-MMC should be smaller than the actual one.

Finally, characteristics of wire-MMC are compared with those of the tapes fabricated from mechanically alloyed powder (tape-MA) reported by Herrmann et al [20] and Hääler et al [40]. For both wire-MMC and tape-MA, the densification of microstructure is achieved, and the practical value of $J_c$ over $10^3$ A mm$^{-2}$ is obtained at 4.2 K and 7–8 T. On the other hand, the energy transferred to powder during milling, $E_m$, which is estimated from the formula by Hääler et al [41], is quite different. The values of $E_m$ per mass of powder are estimated to be in order of $10^4$ J kg$^{-1}$ and $10^3$ J kg$^{-1}$ for wire-MMC and tape-MA, respectively. In tape-MA, owing to high $E_m$, an MgB$_2$ phase is generated at a volume fraction of several dozen percent during milling [41]. The generation of MgB$_2$ should partially contribute to the densification of the microstructure because the increase in the fraction of MgB$_2$ in precursor powder reduces $\Delta \nu$ in equation (1) and increases $P$. Thus, the mechanism for the densification of microstructure in wire-MMC is not completely the same as that in tape-MA. The mechanism for the excellent $J_c$ of wire-MMC is not completely the same as that of tape-MA either. Tape-MA has anisotropic $B_{c2}$ and $J_c$ depending on the magnetic field direction because the $ab$
planes of MgB$_2$ grains are partially aligned parallel to the tape surface [42, 43]. In the case of tape-MA, thus, not only the dense microstructure but also the partial alignment of MgB$_2$ grains should contribute to the excellent $J_c$ in magnetic fields parallel to the tape surface.

4. Conclusion

A high-performance mono-filamentary MgB$_2$ wire was successfully fabricated by using the precursor powder prepared by mechanical milling of magnesium, boron, and coronene powders. This characteristic precursor powder, in which nano-sized boron particles are dispersed in a magnesium matrix, led to the densification of the MgB$_2$ filament, and the limitation of the critical current density that occurs in the case of the typical in situ process was overcome. As a result, the wire fabricated from mechanically milled powder had higher critical current density than state-of-the-art wires in wide temperature and magnetic field ranges.

Acknowledgments

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References


Table 2. Lattice constants, packing factor, and electromagnetic properties of MgB$_2$ filaments.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Lattice constants (nm)$^a$</th>
<th>$P$</th>
<th>$K$</th>
<th>$\rho_0$ ($\mu\Omega$ cm)</th>
<th>$T_c$ (K)</th>
<th>$B_{c2}$ (20 K) (T)$^b$</th>
<th>$J_c$ ($10^3$ A m$^{-2}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire-MMC</td>
<td>0.3081</td>
<td>0.3522</td>
<td>0.82</td>
<td>0.35</td>
<td>12.19</td>
<td>35.4</td>
<td>12.94</td>
</tr>
<tr>
<td>Wire-IN</td>
<td>0.3087</td>
<td>0.3524</td>
<td>0.60</td>
<td>0.22</td>
<td>6.15</td>
<td>36.8</td>
<td>11.6</td>
</tr>
<tr>
<td>Wire-INC</td>
<td>0.3078</td>
<td>0.3524</td>
<td>0.63</td>
<td>—</td>
<td>—</td>
<td>35.9</td>
<td>14.51</td>
</tr>
</tbody>
</table>

$^a$ Estimated from x-ray diffraction profiles in figure 3.
$^b$ To estimate $B_{c2}$ at 20 K, $B_{c2}–T$ curve is linearly extrapolated.
$^c$ Estimated from magnetization curve.


