Microstructural and crystallographic imperfections of MgB2 superconducting wire and their correlation with the critical current density

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Keywords
their, wire, microstructural, crystallographic, density, imperfections, current, critical, mgb2, correlation, superconducting

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I. INTRODUCTION

The synthesis of MgB$_2$ material at low sintering temperature keeps the grain size small, which leads to a strong enhancement of pinning.¹ Nevertheless, 30–40% void content, resulting in severe degradation of critical current, is still hard to avoid in the in-situ process.² Such a drawback indicates that there is still room to further enhance the superconducting performance, especially the critical current. In early works of Flukiger³ and Tanaka,⁴ it was shown that core or packing density is strongly related to the critical current. It was further reported that the porosities or voids hindered grain connectivity, and are apparently argued to be the prime cause for reduced critical current. A direct way to eliminate the void formation, the internal Mg diffusion method,⁵–⁸ has been developed, and denser wires and bulks can be fabricated. Nevertheless, a central void area due to the Kirkendall effect of magnesium still remains one of disadvantages in terms of commercialization. According to the recent literature,⁹ the void fraction is significantly diminished by homogeneous carbon capping.

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as an alternative method, approaching the theoretical limit of 30% voids, which exactly corresponds to the increase in the measured low field critical current density. It is to be noted, however, that the performance of such MgB$_2$ is still far below the depairing current density of MgB$_2$.

The major challenge is how to improve grain connectivity or how to remove voids to further raise the critical current without electrical dissipation. To achieve this, the structural or microscopic origin for the enhancement needs to be studied in depth.$^{10-15}$ MgB$_2$ is a two-band superconductor, and the superconducting properties can be greatly influenced in various ways that depend on this, for example, by microstructural imperfections.$^{16-21}$ but there is no consensus as yet, mainly because of difficulties in obtaining atomic-scale transmission electron microscope (TEM) images. In this study, as an extension to studies on MgB$_2$ wire, the variation of various structural parameters and defects has been extensively evaluated and is discussed with the critical current performance. We clarify that the structural or microscopic mechanism arises from intrinsic defects and a resulting increase in the impurity scattering rate.

II. EXPERIMENTAL PROCEDURE

MgB$_2$ wire was fabricated by the in-situ power-in-tube process. Magnesium (Mg, 99.9%, 325 mesh) and boron (B, 99.8%, 1 $\mu$m) powders were used as starting materials with the composition of Mg : B = 1 : 2. The mixed powders were put into an iron (Fe) tube with a length of 140 mm. The Fe tube had an outer diameter (O.D.) of 10 mm and an inner diameter (I.D.) of 8 mm. The composite was drawn down to an O.D. of 0.8 mm. The fabricated wires were then wrapped in Zr foil and sintered at 650 to 1000 $^\circ$C for 30 min under high purity argon (Ar, 99.9%) gas. All samples were initially characterized by detailed X-ray diffraction analysis. The morphology and microstructure were characterized by field emission-scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Transport measurements to determine resistivity ($\rho$) were carried out by the standard ac four-probe method. Transport critical current ($J_c$) was characterized by the standard four-probe method with the criterion of 1 $\mu$Vcm$^{-1}$. In the case of the irreversibility field ($B_{irr}$), two kinds of criteria were applied: 1) $B_{irr}$ was defined at a $J_c$ (or $I_c$) criterion of 100 Acm$^{-2}$ (or 0.1 A), as obtained from a linear extrapolation of the field dependence of the critical current density (or critical current) and 2) $B_{irr}(T)$ was defined as the field where the temperature dependent resistance at constant magnetic field, R($H_{irr}$, $T$) = 0.1$R_{ns}$, with $R_{ns}$ being the normal state resistance at 40 K.

III. RESULTS AND DISCUSSION

MgB$_2$ phase is known to start to form from 580 $^\circ$C under Ar atmosphere.$^{22}$ Two exothermal peaks are commonly observed. The first peak around 450 $^\circ$C might be related to the MgO formation due to a reaction between Mg and B$_2$O$_3$. B$_2$O$_3$ is known to melt around this temperature. The second peak around 600 $^\circ$C is attributed to the MgB$_2$ formation. Based on this study, we thus sintered the MgB$_2$ wire at 650 $^\circ$C for 30 min as a reference, and the structural analysis of this MgB$_2$ wire was directly confirmed by high-energy synchrotron radiation (SR) powder diffraction using a large Debye-Scherrer camera equipped with an imaging plate as a highly sensitive X-ray detector, at an experimental hutch of SPring-8, Japan. The SR diffraction pattern is shown in Figure 1. To obtain more information, the Rietveld refinement of the crystal structure was carefully carried out with the RIETAN-2000 program.$^{23}$ As shown in Table I, the $a$- and $c$-axis lattice parameters were estimated to be 3.0832(2) Å and 3.5221(2) Å, respectively, which are consistent with the literature.$^{24}$ In general, the results of refinement can be assumed to be reliable when the value of $\chi^2$ (goodness of fit) is under 1.69.$^{25}$ This means that our calculation is quite reasonable. Peak broadening, which is caused by smaller size crystallites or subgrains, and microstrain within the crystal lattice, was also analyzed using an asymmetric pseudo-Voigt function.$^{26}$ The calculated crystallite size was 44 nm, and lattice strain was 0.34%. This induced strain directly affects the impurity scattering between the $\pi$ and $\sigma$ bands of MgB$_2$.$^{27}$ Interestingly, a large fraction of MgO (7–10% mass fraction) still existed in our samples. Spherical MgO particles 30–40 nm in size were obviously observed along the [011] beam orientation, and one of these is shown in Figure 2. The fast Fourier transform (FFT) pattern and electron energy loss spectrum (EELS) in Fig. 2 are obviously confirmed. It is believed that the
FIG. 1. High-energy SR diffraction pattern of pure MgB$_2$ wire sintered at 650°C for 30 min. The markers indicate the Bragg peak positions for MgB$_2$ and MgO, respectively.

TABLE I. Results of Rietveld refinement on the XRD data.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Hexagonal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P6/mmm</td>
</tr>
<tr>
<td>SR powder diffraction experiment</td>
<td>Synchrotron</td>
</tr>
<tr>
<td>Radiation source</td>
<td>0.499902 (2)</td>
</tr>
<tr>
<td>$\Delta 2\theta$ (°)</td>
<td>0.01</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>300</td>
</tr>
<tr>
<td>Reliability factors and goodness of fit</td>
<td></td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>2.23</td>
</tr>
<tr>
<td>$R_p$ (%)</td>
<td>1.74</td>
</tr>
<tr>
<td>$R_B$ (%)</td>
<td>1.82</td>
</tr>
<tr>
<td>$R_F$ (%)</td>
<td>0.9</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.93</td>
</tr>
<tr>
<td>Lattice parameters and unit-cell volume</td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>3.0832 (2)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>3.5221 (2)</td>
</tr>
<tr>
<td>$V$ ($\text{Å}^3$)</td>
<td>28.997 (3)</td>
</tr>
<tr>
<td>Peak broadening parameters</td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>0.058 (1)</td>
</tr>
<tr>
<td>$Y$</td>
<td>0.262 (36)</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>44 (1)</td>
</tr>
<tr>
<td>Lattice distortion (%)</td>
<td>0.34 (6)</td>
</tr>
</tbody>
</table>

The presence of nano-MgO precipitates in the MgB$_2$ polycrystalline grains is a common structural feature that has its origin in the magnesium powder. With regards to role of the MgO particles, however, there is still controversy from the viewpoint of flux pinning. If the MgO particles have a homogeneous small size ($<10$ nm), they would be helpful for enhancing the pinning. In contrast, large-size MgO particles could act as an impurity phase, causing poor connectivity between grains.

In order to evaluate the effects of grain connectivity in depth, we sintered three wire samples at different sintering temperatures (650, 800, and 1000°C) for a comparative study. The...
onset transition temperatures of the corresponding MgB$_2$ wires are estimated to be 37.5, 37.9, and 38.8 K, respectively, as shown in Figure 3. With increasing sintering temperature, the critical transition temperature increased. The lower transition temperature observed in our sample sintered at 650 °C might be related to the strong impurity scattering between the $\pi$ and $\sigma$ bands of MgB$_2$, which is caused by crystalline imperfections, that is, a high degree of lattice disorder. The correlation between the lattice strain and the transition temperature was first reported by Serquis et al.$^{31}$ Lattice disorder also can influence the resistivity and the critical current density.$^{27}$ It is generally argued that the residual resistivity, $\rho_{40K}$, is related to the intragrain impurity scattering, whereas the difference between the residual resistivity and the room temperature resistivity, $\Delta \rho = \rho_{300K} - \rho_{40K}$, is affected by intergrain scattering.$^{32}$ In particular, the quantitative value of the residual resistivity seems to be closely correlated with the impurity scattering between the $\pi$ and $\sigma$ bands, resulting in the observed lower transition temperature.
in the close correlation with the critical temperature. Importantly, the active cross-sectional area fraction (AF)\(^3\) is usually defined as, \( \text{AF} = \Delta \rho_{\text{ideal}} / (\rho_{300 \text{ K}} - \rho_{40 \text{ K}}) \), where \( \rho_{40 \text{ K}} \) and \( \rho_{300 \text{ K}} \) are the resistivity measured at 40 K and 300 K, respectively. \( \Delta \rho_{\text{ideal}} \) is the resistivity difference between 40 K and 300 K for an ideal sample, and the value of 7.3 \( \mu \Omega \) cm is typically used.\(^3\) From the resistivity measurements, the AF values were found to be 25.3, 24.7, and 21.4\%, respectively, with increasing sintering temperature. It is to be noted that the grain connectivity represented by the AF become poorer. This is because the amount of voids or porosities due to Mg evaporation increases with increasing sintering temperature. Clearly, the AF of our wires fabricated by the powder-in-tube (PIT) process is still far below that for well-connected MgB\(_2\) thin films.\(^3\) From the viewpoint of the grain connectivity, a low temperature sintering process would be beneficial. Beside this, a low critical temperature is also known to be associated with grains that are kept small to improve the pinning or critical current density. Moreover, the broadening of the transition temperature was found to become larger with increasing external magnetic field up to 8.7 T, as shown in Figure 4. In particular, the wire sintered at high temperature had a transition with a much longer tail at 8.7 T. This is probably due to thermally activated flux creep or flow.\(^3\) From these viewpoints, wire sintered at low temperature will be considered for further studies. The wire sintered at 650 °C for 30 min under Ar is expected to exhibit the best critical current density.

Critical current densities measured at different operating temperatures (4.2 K–30 K) are shown in Figure 5(a). At 10 T and 4.2 K, the critical current density was estimated to be 3,000 A/cm\(^2\), which is comparable to the values in previous reports.\(^3\) In addition, the critical current density exceeds 10\(^5\) A/cm\(^2\) at 4 T and 4.2 K, and the corresponding value is more than 10\(^4\) A/cm\(^2\) at 20 K. The field dependence of the critical current density or critical current (Figure 5(b)) can be numerically fitted by the following integral equation:\(^2\)\(^7\),\(^3\)

\[
J_c = \int_0^\infty \left( \frac{p(J) - P_c}{1 - P_c} \right)^{1.79} dJ
\]

where \( p(J) \) is the fraction of grains with critical current density above \( J \) and \( P_c \) is the percolation threshold, the minimum fraction required for a superconducting current flow. The critical current of each grain is calculated with a grain boundary pinning model: \( J_g = F_m \cdot (1 - B / B_{c2})^2 / \sqrt{B_{c2}^2 B} \), where \( F_m \) is the pinning force maximum. The upper critical field, \( B_{c2} \), has an angular dependence, which can be described by: \( B_{c2}(\theta) = B_{c2}^\theta / \sqrt{\gamma^2 \cos^2(\theta) + \sin^2(\theta)} \), from the anisotropic Ginzburg-Landau theory. Here, only four fitting parameters, the upper critical field (\( B_{c2} \)), the anisotropy parameter (\( \gamma \)), the pinning force maximum (\( F_m \)), and the percolation threshold (\( P_c \)) are needed to
describe the field dependence of the critical current for each temperature. We previously reported that for polycrystalline wire samples, the percolation threshold, $P_c$, is usually 0.26, and that value was used in this work as well.9, 20, 27 The best fitting parameters are listed in Table II, and the corresponding fitting curves are shown together in Figure 5(b).

For practical applications, the temperature dependence of the irreversibility field ($B_{irr}$) for the MgB$_2$ is also of importance, as shown in Figure 6. Two different kinds of criteria are applied to estimate $B_{irr}$. It can be observed that the estimated values from the resistivity are larger than from the critical current density. This is probably due to the differences between the ac and dc transport measurements. The general trend is similar, however, as a function of operating temperature. We also can estimate the irreversibility field from the Kramer plot, as shown in inset of Figure 6. According to the Kramer plots, the pinning force, $F_p = I_c^{1/2} \times B^{1/4}$, is expected to be a linear function of field. Long tails at the offset in the measured data were observed, however. This method for the determination of the irreversibility field might be underestimating it, in view of the actual upper critical field. Another interesting feature is the strong relationship between the upper critical field and the irreversibility field. The irreversibility field is commonly known to be enhanced by...
inducing structural defects, such as distortion and poor crystallinity. In addition, an increase in the upper critical field affects the irreversibility field. In our study, superior superconducting properties, especially the field dependence of the critical current density, can be governed by the larger upper critical field from imperfections in the crystalline structure, as well as the strong pinning from small grains. Therefore, structural imperfections are very crucial for superior critical current density. The structural imperfections are known to be induced by both carbon doping and the low temperature sintering process. It is very difficult, however, to reduce the voids.

Figure 7 shows SEM images of polished core surface for samples sintered at 650 °C, 800 °C, and 1000 °C for 30 min. As can be seen in the images, porosities/voids remained the sample, regardless of sintering temperatures. Voids were present due to mainly Mg melting. This phenomenon occurs because melted magnesium at around 650 °C starts to diffuse into solid amorphous boron. As a result, voids normally reduce the active superconducting area and the current transport paths. In order to obtain more clues, the microstructure near voids is further observed by scanning TEM (STEM) image and energy dispersive X-ray (EDX) spectroscopy elemental mapping, as can be seen in Figure 8. Very interestingly, oxygen (O) surrounding voids are obviously found as a thin layer, indicating existence of MgO. Since voids were originally obtained from spaces of Mg powders. That is, residual Mg near by the voids would be oxidized to form MgO. It is noted that MgO

![Graph](image-url)

**FIG. 5.** Field dependence of (a) the critical current density and (b) the critical current for wire sintered at 650 °C for 30 min at different operating temperatures of 4.2, 10, 15, 20, 25, and 30 K. All fitting lines of Figure 5(b) are calculated using the percolation model.

**TABLE II.** Percolation model fitting parameters.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$F_0$ (ATcm$^{-2}$)</th>
<th>$B_{c2}$ (T)</th>
<th>Gamma ($\gamma$)</th>
<th>$P_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>3767123</td>
<td>24.7</td>
<td>4</td>
<td>0.26</td>
</tr>
<tr>
<td>10</td>
<td>2739726</td>
<td>17.4</td>
<td>3.1</td>
<td>0.26</td>
</tr>
<tr>
<td>15</td>
<td>1815068</td>
<td>12.4</td>
<td>2.4</td>
<td>0.26</td>
</tr>
<tr>
<td>20</td>
<td>1232877</td>
<td>9.45</td>
<td>2.33</td>
<td>0.26</td>
</tr>
<tr>
<td>25</td>
<td>582192</td>
<td>6.45</td>
<td>2.2</td>
<td>0.26</td>
</tr>
<tr>
<td>30</td>
<td>102740</td>
<td>4.05</td>
<td>2.1</td>
<td>0.26</td>
</tr>
</tbody>
</table>
FIG. 6. Temperature dependence of the irreversibility field ($B_{irr}$) of wire sintered at 650 °C for 30 min. Inset shows the Kramer plots at different temperatures.

FIG. 7. SEM images of polished core surface for samples sintered at 650 °C, 800 °C, and 1000 °C.
particles segregated near voids severely degrade the connectivity between crystalline MgB$_2$ grains and shorten current transport paths. From this observation, it is expected that dense MgB$_2$ core, without voids or porosities, can bring superior critical current. Moreover residual boron powders are still remained even after sintering process, as can be seen in Figure 9. For this, STEM image and EDX spectroscopy were again used. Coarse crystalline MgB$_2$ grains are found to be blocked by the residual boron powders, thereby degradation of the current transport paths as well. Therefore, we believe that the elimination of the voids and residual boron powders is very important to further improve the transport critical current of MgB$_2$ superconductor for practical applications.

As can be seen in Figure 10, a large fraction of MgO particles are randomly existed because MgO formation could easily take place before MgB$_2$ is formed. This indicates that the MgO formation
yields deficient magnesium, resulting in residual boron powders (Figure 9). Thus reducing exposure to oxygen plays an important role in this MgB₂ system. Alternatively, excess magnesium, which can compensate the magnesium deficiency due to the MgO formation, would be effective way to reduce residual boron powders in the MgB₂ matrix.

IV. CONCLUSIONS

In summary, detailed structural analysis has been conducted on MgB₂ superconducting wire sintered at various temperatures. It was found that the lower transition temperature due to low sintering temperature is related to higher impurity scattering between the \( \pi \) and \( \sigma \) bands of MgB₂ caused by high lattice disorder and crystalline imperfections. Strong impurity scattering causes a larger upper critical field, and thereby, increases the critical current density. Moreover, the low sintering temperature keeps the grain size small, which strongly enhances pinning. To further enhance in-field critical current density, the voids or porosities, which block transport current paths, need to be decreased. Our comprehensive studies provide atomic-level insights that can pave the way for enhancing transport critical current to meet the requirements of practical applications.

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