In-field Jc improvement by oxygen-free pyrene gas diffusion into highly dense MgB2 superconductor

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Abstract
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Keywords
field, improvement, oxygen, free, pyrene, gas, diffusion, into, highly, dense, MgB2, superconductor

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In-field $J_c$ improvement by oxygen-free pyrene gas diffusion into highly dense MgB$_2$ superconductor

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Oxygen-free pyrene gas as a carbon (C) dopant was delinked and incorporated into highly dense MgB$_2$ structure via a gas phase diffusion method. The technique offers the advantages that molecular C is homogeneously distributed into MgB$_2$ and substituted at the boron sites without any severe deterioration of grain connectivity. The C substitution causes a significant shrinkage of the $a$-lattice parameter and an increase in the lattice strain, resulting in high disorder. The introduction of structural disorder as a result of C doping leads to a considerable enhancement of the in-field critical current density ($J_c$) and upper critical field. © 2011 American Institute of Physics. [doi:10.1063/1.3532033]

I. INTRODUCTION

MgB$_2$ is one of the most promising materials for the next generation of superconducting applications because of its high critical transition temperature ($T_c$) of 39 K (Ref. 1) and lack of weak-links at grain boundaries. However, the in-field critical current density ($J_c$) still needs to be further improved at its higher operating temperature of 20 K. In order to achieve this, issues of the grain connectivity and the carbon (C) incorporation into MgB$_2$ material should be addressed. These include (i) grain coupling, (ii) effective cross-sectional area, (iii) impurity phase fraction that disturbs current-flow, and (iv) homogeneous C incorporation into the MgB$_2$ lattice structure.

Homogeneous C incorporation is a critical issue for high magnetic field applications of MgB$_2$. Lattice disorder increases due to C substitution, which causes an enhancement in the upper critical field ($B_{c2}$) and high-field $J_c$.$^{3,4}$ In contrast, the $J_c$ in self-field decreases because of residual impurity phase and the reduction in effective cross-sectional area. So far, many groups have focused on solid and/or liquid mixing as a processing method for improving the efficiency of C incorporation.$^{5-9}$ In particular, the aim of the liquid process is to achieve better mixing among the starting materials. However, agglomeration of unreacted C still exists at the grain boundaries, even after the sintering process. Here, we suggest a method of C substitution via gaseous phase diffusion. The C distribution can be easily achieved by this method and it can be applied widely to bulk, wire, and thin film fabrications for enhancement of $J_c$.

In our earlier study,$^{10,11}$ two-step processing via magnesio-
For estimating accurate structural parameters from the Rietveld refinement, high-energy synchrotron radiation (SR) powder diffraction experiments were carried out at the SPring-8 facility in Japan. All samples were also characterized by $T_c$, $J_c$, and $B_{c2}$ from magnetic measurements. $T_c$ was determined by ac susceptibility measurements at $f = 76.97$ Hz with $\mu_0H_{ac} = 50$ $\mu$T. $J_c$ was calculated from the magnetization hysteresis loops using the Bean critical state model. In addition, $B_{c2}$ was derived from ac susceptibility with $f = 76.97$ Hz, $\mu_0H_{ac} = 50$ $\mu$T, and $\mu_0H_{ac} = 0$, 0.2, 0.5, 1, 3, and 5 T. Scanning transmission electron microscopy (STEM) was employed to analyze the morphology, structure, and phase composition.

### III. RESULTS AND DISCUSSION

The changes in the lattice parameters with the two different sample preparation methods are presented in Table I. The Rietveld refinement of the crystal structure was carried out with the RIETAN-2000 program. The asymmetric pseudo-Voigt function was used to investigate peak broadening effects caused by crystallite size and microstrain in the crystal lattice. As mentioned in our previous works, shrinkage of the $a$-lattice parameter would be strong evidence for C substitution. Interestingly, $a$-lattice parameters for studies 1 and 2 decreased from 3.0834 Å to 3.0713 Å and 3.0756 Å, respectively. It is well known that the actual amount of C can

![Diagram of Mg diffusion method](image)

FIG. 1. (Color online) Schematic of Mg diffusion method in combination with pyrene gas treatment used in study 1 and study 2. The sealed Ta tubes were vacuum-sealed in quartz tubes, sintered at 1100 °C for 4 min followed by annealing at 660–710 °C for 24–48 h.

The proper amount of pyrene in the two studies was chosen to be 2.5 wt% of total MgB$_2$, because a small quantity of pyrene is sufficient to provide the required amount of C to significantly improve $J_c$. For reference, an un-doped sample was also prepared from the same Mg diffusion process. Here, Mg ingots (99.9%, 3–5 mm) and amorphous B powder (99.9%, 1 $\mu$m) were used as the starting materials. Doped and un-doped samples were sintered for a short period of 4 min at 1100 °C first, followed by the second sintering conditions, namely, 660–710 °C for 24–48 h and 660 °C for 14 h, respectively.

<table>
<thead>
<tr>
<th>SR powder diffraction experiment</th>
<th>Study 1</th>
<th>Study 2</th>
<th>un-doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation source</td>
<td>$\lambda$ (Å)</td>
<td>$\Delta 2\theta$ (°)</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>Synchrotron</td>
<td>0.49919 (5)</td>
<td>0.49901 (2)</td>
<td>0.01</td>
</tr>
<tr>
<td>Reliability factors</td>
<td>$R_{wp}$</td>
<td>$R_p$</td>
<td>$R_I$</td>
</tr>
<tr>
<td>3.74</td>
<td>3.38</td>
<td>3.23</td>
<td>4.22</td>
</tr>
<tr>
<td>Goodness of fit $s$</td>
<td>1.02</td>
<td>1.16</td>
<td>1.23</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td>$V$ (Å$^3$)</td>
</tr>
<tr>
<td>3.0697 (3)</td>
<td>3.0713 (4)</td>
<td>3.0756 (3)</td>
<td>3.0834 (4)</td>
</tr>
<tr>
<td>3.5262 (2)</td>
<td>3.5263 (3)</td>
<td>3.5294 (2)</td>
<td>3.5214 (3)</td>
</tr>
<tr>
<td>Peak broadening coefficients</td>
<td>$X$</td>
<td>$Y$</td>
<td>$X$</td>
</tr>
<tr>
<td>Mass fractions</td>
<td>92.3</td>
<td>93.1</td>
<td>94.7</td>
</tr>
<tr>
<td>MgB$_2$ (%)</td>
<td>7.7</td>
<td>6.9</td>
<td>5.3</td>
</tr>
</tbody>
</table>

For estimating accurate structural parameters from the Rietveld refinement, high-energy synchrotron radiation (SR) powder diffraction experiments were carried out at the SPring-8 facility in Japan. All samples were also characterized by $T_c$, $J_c$, and $B_{c2}$ from magnetic measurements. $T_c$ was determined by ac susceptibility measurements at $f = 76.97$ Hz with $\mu_0H_{ac} = 50$ $\mu$T. $J_c$ was calculated from the magnetization hysteresis loops using the Bean critical state model. In addition, $B_{c2}$ was derived from ac susceptibility with $f = 76.97$ Hz, $\mu_0H_{ac} = 50$ $\mu$T, and $\mu_0H_{ac} = 0$, 0.2, 0.5, 1, 3, and 5 T. Scanning transmission electron microscopy (STEM) was employed to analyze the morphology, structure, and phase composition.

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be inferred from the lattice parameters by comparison with the lattice parameters of single crystal. The diffusion process enables C to substitute effectively into the B sites causing significant lattice distortion/disorder. That is to say, the substitution brings lattice strain into the MgB$_2$ due to the difference in atomic radii between C and B. The effective lattice strain is much larger in B layer than that of Mg layer because the effect of C replacing B site will accumulate in lattice strain. The effect may reduce with decreasing temperature with decreasing $T_c$. The normalized curvature near $T_c$ indicates that the diffusivity in the $\sigma$ bands is suppressed compared to that in the $\pi$ bands. As a result, the enhanced $B_{c2}$ provides an indication of increased two-band impurity scattering, most likely due to the lattice strain induced by C substitution. The structural disorder caused by the localized strain would enhance $B_{c2}$, resulting in the enhancement of in-field $J_c$, as shown in Fig. 3.

It is interesting to note that in contrast to the case of any other doping, the self-field $J_c$ at 20 K does not show any difference between the doped and undoped samples. The main reasons are (i) no significant change in the mass fractions of MgB$_2$ and MgO (Table 1) and (ii) the pyrene gas treatment process, i.e., molecular C, does not degrade the connectivity of highly dense MgB$_2$. The active cross sectional area fraction ($A_F$), which is a measure of grain connectivity, can be obtained by

$$A_F = \Delta \rho_{\text{ideal}}(\rho_{300 \, K} - \rho_{40 \, K}),$$

where $\rho_{40 \, K}$ and $\rho_{300 \, K}$ are resistivity values of samples measured at 40 K and 300 K, respectively. $\Delta \rho_{\text{ideal}}$ is resistivity difference between 40 and 300 K for a fully connected sample made from a high purity source, such as a dense filament made by chemical vapor deposition, for which $\Delta \rho_{\text{ideal}}$ is 7.3 $\mu\Omega$ cm. It is well known that a lower value of $\Delta \rho$ indicates good connectivity between grains. Interestingly, $A_F$ of the Mg diffusion sample is comparable to well-connected MgB$_2$ thin film or Mg diffused B whisker. For example, $\Delta \rho$ values of our Mg diffusion samples were estimated to be 9.2–19.0 $\mu\Omega$ cm. Thus, self-field $J_c$ at 20 K reached 10$^6$ Acm$^{-2}$ and in-field $J_c$ at around 5 T showed 10$^4$ Acm$^{-2}$. This result is also comparable to those for MgB$_2$ thin film. To further find other clues, there needs to be deeper insight from the viewpoint of microstructure.

A TEM image of sample 1 is shown in Fig. 4(a). This sample which was first sintered at 1100 °C for 4 min followed by second sintering at 710 °C for 24 h showed the best $J_c$ performance. Interestingly, there seems to be no porosity in the matrix. However, such a bright field (BF)-
which is quite comparable to the performance of MgB2 thin film. Our gas phase diffusion technique offers a useful pro-
tion and impurity phases at grain boundaries are not detected
sions within grains can serve as strong flux pinning centers.

TEM image does not show impurity phases and grain bound-
aries. Therefore, an annular dark field (ADF)-STEM and high
angle ADF (HAADF)-STEM images of the same sample were captured and they are shown in Figs. 4(b) and 4(e). The ADF-STEM image confirmed that there are many
nanoparticles embedded within the MgB2 grains. It is well
known that a HAADF-STEM image displays atomic number
dependent contrast. Therefore, nanoparticles in the MgB2 grains show weak B K and strong O K intensity. Therefore, nanoparticles in the matrix can be related to MgO as shown by green circles [Fig.
4(b)]. The existence of MgO was also confirmed in the high-
energy SR powder diffraction results (Table I).

The presence of MgO nanoparticles could enhance the flux
pinning effect.26,27 Since the coherence length in a-b plane of MgB2 is about 6–7 nm,28 a limited amount of inclu-
sions within grains can serve as strong flux pinning centers.
The most noticeable feature is that unreacted C agglomera-
tion and impurity phases at grain boundaries are not detected
from the EELS maps. This means that our technique of gase-
ous phase diffusion can efficiently incorporate C into MgB2
structure without any deterioration of grain connectivity.

IV. CONCLUSION

We have demonstrated the influence of C-containing gas
on the structural and superconducting properties of highly
dense MgB2 bulks synthesized via diffusion process. The
C-containing gas penetrated into the MgB2 bulks and caused
lattice shrinkage of the a-lattice parameter and high disorder in
the lattice structure, resulting in significant enhancement
of $B_c^2$ and $J_c$. Self-field $J_c$ at 20 K reached $10^6$ A cm$^{-2}$,
which is quite comparable to the performance of MgB2 thin
film. Our gas phase diffusion technique offers a useful pro-
cessing option in various manufacturing processes for MgB2
bulks, wires, and thin films for practical applications.

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