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Effect of sintering temperature on structural defects and superconducting properties in MgB$_2$ + C$_6$H$_6$O$_5$

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Abstract. We report a systematic study on the effect of sintering temperature on the lattice parameters, amount of carbon (C) substitution, microstructure, critical temperature ($T_c$), critical current density ($J_c$), upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$) of 10 wt% Malic acid (C$_6$H$_6$O$_5$) doped MgB$_2$ superconductors. All the samples were heat treated at temperatures ranging from 600 to 900 °C. With increasing the sintering temperature both the a-axis lattice parameter and $T_c$ are decreased compared to un-doped samples, indicating that the C released from C$_6$H$_6$O$_5$ substituted into Boron (B) position resulting in the enhancement of $J_c$, $H_{c2}$ and $H_{irr}$.

1. Introduction

The discovery of superconductivity at 39 K [1] in MgB$_2$ can be applied to a cryogen-free magnet at an operating temperature of around 20 K [2]. The improvements in critical current density ($J_c$), upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$) have been the key topics of research efforts. Gurevich et al. have reported very high $H_{c2}$, up to 50 T, for MgB$_2$ films with high resistivities [3]. They found a correlation between the resistivity and $H_{c2}$ and showed that the remarkable $H_{c2}$ enhancement can be explained in the framework of the two gap superconductivity in MgB$_2$, which provides special opportunities for further enhancement in $H_{c2}$ by tuning the impurity scattering. A significant enhancement in the electromagnetic properties of MgB$_2$ has been achieved through a doping with various forms of carbon (C). For example, the addition of SiC [4-6], C [7, 8], carbon nanotubes (CNTs) [9], carbohydrate (CH) [10] and a liquid additive, silicone oil [20] have been found to be effective in improving the $J_c$-$H$ characteristics of MgB$_2$. In particular, C can enter the MgB$_2$ structure by substituting for B, which leads to increased impurity scattering in the two-band MgB$_2$, and hence significantly increases $J_c$ and the $H_{c2}$. However, the C doping effect for MgB$_2$ superconductor has been limited by the local agglomeration of nano-sized dopant particles. In that case un-reacted C remains in the MgB$_2$ matrix and reacts with Mg or B powders, resulting in the formation of impurity phases. To overcome these properties, it is necessary to study the homogeneity of mixing as well as the activity of the reactions between B and C materials so as to achieve a full reaction. The various methods have been studied by many groups. Mickelson et al. [11] first reported that B$_x$C was considered to be one of the more reactive C-containing compounds because free C was liberated from B$_x$C. However, using B$_x$C compound meant that a higher sintering temperature up to 1200
\(^{\circ}\)C was needed, as well as a longer sintering time. Dou et al. [12] studied the effects of SiC doping on MgB\textsubscript{2} superconductor to overcome the same problems. Even though SiC was much more effective at enhancing the \(J_c\) at a low sintering temperature (\(-650\,^{\circ}\)C), there were agglomerations of nano-particles in the MgB\textsubscript{2} matrix, resulting in blocking of current flow. C and CNT as dopants also require a higher sintering temperature of 900 \(^{\circ}\)C for C substitution to take place. In addition, because of the high aspect ratio, the CNTs were much more easily entangled [13], reducing homogeneity.

In our group we have already shown that \(J_c\) enhancement by more than one order of magnitude in high magnetic field can be achieved with only a slight reduction in \(T_c\) for MgB\textsubscript{2} + C\textsubscript{6}H\textsubscript{12}O\textsubscript{5} [10] sintered at 900 \(^{\circ}\)C. To further explore the potential as a C source of C\textsubscript{6}H\textsubscript{12}O\textsubscript{5} low temperature sintering also has significant advantages for commercial MgB\textsubscript{2} conductors such as MgB\textsubscript{2}+SiC. Recently, Fujii \textit{et al.} [14] prepared Fe-containing MgB\textsubscript{2} tapes at low temperature of 600 \(^{\circ}\)C using MgH\textsubscript{2} instead of Mg powder. The \(H_c^2\) and \(H_m\) enhancement at low sintering temperature is crucial for the selection of various sheath materials and reduction of production costs. For these reasons, C\textsubscript{6}H\textsubscript{12}O\textsubscript{5} is one of the main candidate materials for low sintering temperature processing at 600 \(^{\circ}\)C, as this C source can be fully decomposed at temperatures as low as 300\(^{\circ}\)C.

\section{Experimental}

MgB\textsubscript{2} pellets were prepared by an in-situ process with the addition of 10 wt\% C\textsubscript{6}H\textsubscript{12}O\textsubscript{5}. The fabrication processing of pellet and wire is described in elsewhere [10, 15]. All samples were sintered in a tube furnace at temperatures ranging from 650 to 900\(^{\circ}\)C for 30 min, and at 600 \(^{\circ}\)C for 4 hours under high purity argon gas. The heating rate was 5 \(^{\circ}\)/min. All samples were characterized by X-ray diffraction (XRD), field emission gun-scanning electron microscopy (FEG-SEM), \(T_c\), \(H_m\), and \(H_c^2\). The lattice parameters were obtained from Rietveld refinement. \(T_c\) was defined as the onset temperature at which diamagnetic properties were observed. In addition, \(H_c^2\) and \(H_m\) were defined as \(H_c^2 = 0.9R(T_c)\) and \(H_m = 0.1R(T_c)\) from the resistance (R) versus temperature (T) curve.

\section{Result and discussion}

As shown in Figure. 1, the \(\alpha\)-axis lattice parameter decreases from 3.0851 \(\AA\) for a well developed un-doped sample sintered at 900\(^{\circ}\)C for 30 min to 3.0749, 3.0753, 3.0722, 3.0734, 3.0764 \(\AA\) for MgB\textsubscript{2} + 10 wt\% C\textsubscript{6}H\textsubscript{12}O\textsubscript{5} samples sintered at 600 \(^{\circ}\)C for 4 hours and 650, 700, 800, and 900\(^{\circ}\)C for 30 min, respectively. Even though there are some fluctuations in the changes of the \(\alpha\)-axis lattice parameter for the samples with different sintering temperatures, the amount of C substitution seemed to be saturated in Figure. 2, with an average value of \(x \sim 0.0242\) in the Mg (B\textsubscript{1-x}C\textsubscript{x})\textsubscript{2}, at all sintering temperatures [16]. In general, the shrinkage of the \(\alpha\)-axis is attributed to the substitution of C for B. These results indicate that significant C substitution can be achieved for MgB\textsubscript{2} + 10 wt\% C\textsubscript{6}H\textsubscript{12}O\textsubscript{5}, even with a low sintering temperature regime. Thus the decomposition of C\textsubscript{6}H\textsubscript{12}O\textsubscript{5} produces highly reactive C, allowing it to achieve relatively higher C substitution levels at lower temperature, compared to nano-C, B\textsubscript{4}C, and carbon nano-tube [17].

Figure. 3 shows the \(T_c\) for both doped and un-doped samples which increases with increasing sintering temperatures. This indicates that small grains and imperfect crystallinity exist in samples processed at lower temperatures. Yamamoto \textit{et al.} [18] reported that \(H_m\) can be enhanced by degradation of crystallinity due to a low temperature solid-solid reaction. That is, low crystallinity is primarily responsible for larger \(H_m\) and \(H_c^2\). It should be noted that the \(T_c\) of MgB\textsubscript{2} + 10wt\% C\textsubscript{6}H\textsubscript{12}O\textsubscript{5} samples are relatively lower than those of un-doped MgB\textsubscript{2} over the whole sintering range. This result is related to the lattice disorder due to C substitution into B sites.
Figure 5 shows the magnetic $J_c$ of the un-doped sample and the 10 wt% malic acid-added MgB$_2$ samples as a function of the heat-treatment temperatures. It can be seen that the $J_c$ values of the un-doped sample heat-treated at 900 °C for 30 min are higher than those of the C-doped samples in a low magnetic field region at 20 K but slightly lower at 5 K. As the applied magnetic field increases, a crossover between the un-doped and doped samples exists, and the $J_c$ values of the doped samples were much higher than those of the un-doped sample in the high field ranges, indicating an enhanced flux pinning strength. Meanwhile, it was observed that the magnetic $J_c$ values of the doped samples did not show a significant difference among the different heat-treatment temperatures. This is because C substitution was saturated at high temperature region. Fig. 4 also shows the transport $J_c$ at 4.2 K for un-doped and MgB$_2$ + 10 wt% C$_6$H$_{12}$O$_6$ wires with different heat-treatment temperatures. MgB$_2$ + 10 wt% C$_6$H$_{12}$O$_6$ at 600°C for 4 hrs showed the highest $J_c$ due to poor crystallinity and C substitution.

The temperature dependence of $H_{ir}$ and $H_{c2}$ for all the un-doped and MgB$_2$ + 10wt% C$_6$H$_{12}$O$_6$ samples sintered at different sintering temperatures are shown in Figure 6. We observed that $H_{ir}$ and $H_{c2}$ were depressed systematically as the sintering temperature increased to 900 °C. This indicates that degradation of crystallinity at low temperature can be the driving force for larger $H_{ir}$ and $H_{c2}$, as mentioned above. In addition, the significant C substitution into B sites at a sintering temperature as low as 600 °C may induce disorder on the lattice sites, which can lead to the enhancement of the $H_{ir}$ and $H_{c2}$.

Electrical resistivity ($\rho$) values at 40 K and 300 K and Residual resistivity ratios (RRR, $\rho$300 K/$\rho$40 K) for the un-doped and MgB$_2$ + 10wt% C$_6$H$_{12}$O$_6$ samples are summarized in Table 1. The higher $\rho$ values for the doped MgB$_2$ samples indicate that the impurity scattering is stronger due to a greater C substitution into the B sites [10]. As the heat-treatment temperature increased from 600 °C to 900 °C, the RRR values increased from 1.54 to 1.62. The RRR for the un-doped sample had a higher value of 2.15 than those of the C$_6$H$_{12}$O$_6$ doped samples representing a good crystallinity. For a polycrystalline MgB$_2$, the RRR value reflects a sample’s quality. This may also be related to the grain connectivity factor as well. Rowell [19] suggested that the $\Delta\rho$ ($\rho$300 K - $\rho$40 K) values are very effective in revealing a connectivity factor.

4. Conclusion

We investigated the effects of the heat-treatment temperature on the superconducting properties, structural defects, lattice parameters, actual C substitution amount, $T_c$, $J_c$, $H_{c2}$ and $H_{ir}$ for 10 wt% C$_6$H$_{12}$O$_6$ doped MgB$_2$ bulk and wires. With increasing the sintering temperature, both the a-axis lattice parameter and $T_c$ are decreased compared to un-doped samples, indicating that the C released from C$_6$H$_{12}$O$_6$ substituted into B position resulting in the enhancement of $J_c$, $H_{c2}$ and $H_{ir}$.

5. Acknowledgement

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References:

Table 1. Measured resistivity data for un-doped MgB$_2$ and 10wt% C$_6$H$_4$O$_3$ samples with different sintering conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering Conditions (°C)</th>
<th>$\rho$40 K (µΩcm)</th>
<th>$\rho$300 K (µΩcm)</th>
<th>$RRR = \rho$300 K/ $\rho$40 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-doped</td>
<td>650 °C × 30min</td>
<td>41.8</td>
<td>89.87</td>
<td>2.15</td>
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<tr>
<td>Un-doped</td>
<td>900 °C × 30min</td>
<td>24.8</td>
<td>52.08</td>
<td>2.10</td>
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<tr>
<td>MgB$_2$ + C$_6$H$_4$O$_3$</td>
<td>600 °C × 4 hrs</td>
<td>137.1</td>
<td>210.63</td>
<td>1.54</td>
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<tr>
<td>MgB$_2$ + C$_6$H$_4$O$_3$</td>
<td>650 °C × 30min</td>
<td>116.6</td>
<td>152.89</td>
<td>1.31</td>
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<tr>
<td>MgB$_2$ + C$_6$H$_4$O$_3$</td>
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<td>88.9</td>
<td>136.48</td>
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<tr>
<td>MgB$_2$ + C$_6$H$_4$O$_3$</td>
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<td>94.8</td>
<td>144.67</td>
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<tr>
<td>MgB$_2$ + C$_6$H$_4$O$_3$</td>
<td>900 °C × 30min</td>
<td>90.2</td>
<td>146.50</td>
<td>1.62</td>
</tr>
</tbody>
</table>
Figure 1. The α-axis lattice parameters for referenced un-doped MgB$_2$ sintered from 650 °C to 900 °C for 30 min and MgB$_2$ + 10wt% C$_6$H$_5$O$_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).

Figure 2. The amount of C substitution (x) in the Mg (B$_{1-x}$C$_x$)$_2$ for MgB$_2$ + 10wt% C$_6$H$_5$O$_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).

Figure 3. The $T_c$ for referenced un-doped MgB$_2$ sintered from 650 °C to 900 °C for 30 min and MgB$_2$ + 10wt% C$_6$H$_5$O$_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).

Figure 4. The transport $J_c$ at 4.2 K for referenced un-doped MgB$_2$ wire sintered at 650 °C for 30 min and MgB$_2$ + 10wt% C$_6$H$_5$O$_5$ wires sintered at 600 (4 hrs) and 650 °C (30 min).
Figure 5. The $J_c$ at 5 K and 20 K for referenced un-doped MgB$_2$ sintered at 900 °C for 30 min and MgB$_2$ + 10wt% Ca$_2$H$_2$O$_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).

Figure 6. Temperature dependence of normalized $H_{c2}$ and $H_{c1}$ for referenced un-doped MgB$_2$ sintered at 900 °C for 30 min and MgB$_2$ + 10wt% Ca$_2$H$_2$O$_5$ samples sintered from 600 (4 hrs) to 900 °C (30 min).