2009

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http://ro.uow.edu.au/engpapers/3680

Publication Details

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This journal article is available at Research Online: http://ro.uow.edu.au/engpapers/3680
Influence of Heat Treatment on Superconductivity of MgB$_2$
Bulk Sintered in Flowing Welding Grade Ar Atmosphere

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In this paper, MgB$_2$ samples were sintered in flowing welding grade Ar. The effect of the sintering time varying from 10 minutes to 3 hours on superconductivity of MgB$_2$ has been investigated. It has been found that both $H_{c2}$ and $H_{c1}$ increase with the sintering time and they have linear relationships with microstrain. The sample sintered for 30 min exhibits the highest $J_c$ at high fields. The reason can be attributed to the improved connectivity and the increased $H_{c2}$.

Index Terms—MgB$_2$, microstrain, sintering time, superconductivity.

I. INTRODUCTION

The critical current density $J_c$ of MgB$_2$ is the most crucial quantity for use in commercial applications. $J_c$ behavior of MgB$_2$ will be affected by not only processing conditions such as the precursor powders [1]–[6], the heating and cooling rate [7], and the processing temperature and duration [8], as well as the atmosphere [9] but also chemical doping [10]–[13]. Enormous efforts have been made to improve the critical current density, $J_c$, in MgB$_2$ through chemical doping. Among these doping elements, oxygen represents a special case, as nearly all types of MgB$_2$ materials have been treated in a protected atmosphere such as Ar. Oxygen alloying into MgB$_2$ reduced the critical temperature, $T_c$, but improved flux pinning in thin films [14]–[16] and bulks [17]. Recently, Senkowicz et al. have reported the effect of different amounts of exposure time to air during the ball-milling process for pre-reacted MgB$_2$ powder, which was used to prepare MgB$_2$ bulk or wires by the ex situ method [18]. In this case, the effect of atmosphere is limited to the commercially available pre-reacted MgB$_2$. Currently, our group studies the effect of different amounts of exposure time to air during the reaction. Pre-reacted MgB$_2$ pellets have been prepared by the Philips PW1730 Model diffractometer using Cu K$_\alpha$ radiation. Magnetic measurements of the samples were conducted in a commercial Quantum Design Physical Properties Measurement System (PPMS) after they had been polished into a cuboid shape for measurements. Their dimensions were accurately measured with a digital micrometer. The DC magnetic response was obtained in an applied low field of 1 Oe using the conventional zero-field-cooled (ZFC) and field-cooled (FC) procedures. The resistivity as a function of temperature and magnetic field was measured using a four-probe measurement technique.

II. EXPERIMENTAL DETAILS

MgB$_2$ pellet samples were prepared by in situ reaction method which has been previously described in detail [10]. Powders of magnesium (99%) and amorphous boron (99%) with the stoichiometry of MgB$_2$ were well mixed. The mixed powder was pressed under a pressure of 5 tons in a hydraulic press, packed into a Fe tube without sealing, heated to 700°C, and then held for 10 minutes, 30 minutes, and 3 hours in flowing welding grade Ar (99.995%). The samples sintered for 10 min, 30 min and 3 h are termed as samples A, B, and C, respectively, in the following context. The reason for the use of the processing parameters of 700°C is because these are optimal conditions to achieve the best $J_c$(H) performance, based on our previous study [8]. Although heat treatment at 900°C or higher can achieve optimal $T_c$ [8], [22]–[24], this does not provide optimal conditions for $J_c$(H) performance [8]. The Fe tubes were only used as sample holders. They had a diameter of 12 mm and a length of 20 mm, with the two ends open so that Ar could freely flow through the samples. The sintering was followed by furnace cooling to room temperature. Phase analysis was carried out by X-ray diffraction (XRD) in a Philips PW1730 Model diffractometer using Cu K$_\alpha$ radiation. Magnetic measurements of the samples were conducted in a commercial Quantum Design Physical Properties Measurement System (PPMS) after they had been polished into a cuboid shape for measurements. Their dimensions were accurately measured with a digital micrometer. The DC magnetic response was obtained in an applied low field of 1 Oe using the conventional zero-field-cooled (ZFC) and field-cooled (FC) procedures. The resistivity as a function of temperature and magnetic field was measured using a four-probe measurement technique.

III. RESULTS AND DISCUSSION

The XRD patterns for MgB$_2$ samples processed under different annealing times are shown in Fig. 1. As can be seen, all samples show high-purity MgB$_2$ phase with MgO as a minor impurity phase. There is a small amount of MgB$_4$ in sample A. The Rietveld refinement method was performed to analyse the XRD measurements. The refined parameters include the weight

Manuscript received October 16, 2008. Current version published May 20, 2009. Corresponding author: Y. Zhang (e-mail: yz268@uow.edu.au).
Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.
Digital Object Identifier 10.1109/TMAG.2009.2018924
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grains of the superconducting electrons. This will increase the coherence length ($\xi$) due to the relation: $1/\xi = 1/\xi_0 + 1/I$, where $\xi_0$ is the value of $\xi$ for the pure superconductor. According to $H_{c2} = \Phi_0/(2\pi\mu_0\xi^2)$, where $\Phi_0$ is the superconducting flux quantum and $\mu_0$ is the magnetic permeability, $H_{c2}$ will decrease as $\xi$ increases.

Fig. 4 shows the $J_c$($H$) curves for the three samples at 5 K and 20 K. It can be seen that the $J_c$ performance in sample B shows a

fraction of each phase, the lattice parameters of MgB$_2$ and the microstrain. They are shown in Table I.

From Table I it can be seen that as the sintering time increases from 10 min to 30 min, lattice parameters $a$ and $c$ decreases. Lattice parameter $a$ of sample B has been reduced below the ideal value ($a = 3.083 \, \text{Å}$). This indicates that oxygen atoms have diffused into the MgB$_2$ lattice. They may squeeze into the lattice as the interstitial atoms or replace the boron atoms to form MgB$_{2-x}$O$_x$ precipitates [21], leading to the reduced lattice parameters. Since the diffusion density of the oxygen atom increases with the sintering time, the lattice parameters decreases from sample A to sample B. However, when the sintering time is further increased, the diffused oxygen atoms saturate and part of them react with Mg atoms to form MgO for long sintering time (3 hours in sample C). Table I has shown that the fraction of MgO increases when the sintering time increases from 30 min to 3 hours. The reaction of the diffused oxygen atoms and Mg atoms reduces the interstitial oxygen atoms and induce the Mg deficiency, both of which result in the increased lattice parameters in sample C as shown in Table I.

$T_c$'s are listed in Table I. Sample B has a smallest value. $T_c$ varies within a small range of 0.5 K. This indicates that the sintering time does not significantly affect $T_c$. Fig. 2 shows the resistivity-temperature curves for the three samples. The resistivity ($\rho$) for sample C is the largest among samples. The values of $\rho_{40 \, \text{K}}$ and $\rho_{300 \, \text{K}}$ are collected from Fig. 2 and listed in Table I. Sample B exhibits the smallest $\rho_{40 \, \text{K}}$ and $\rho_{300 \, \text{K}}$ whereas sample C has the largest value. The values for $\rho_{40 \, \text{K}}$ listed in Table I are higher than the single crystal (5.3 $\mu\Omega$cm, [25]) and the dense filament made by chemical vapor deposition (CVD) (7.3 $\mu\Omega$cm, [26]). The reason can be attributed to poor connectivity in the studied samples. The XRD patterns in Fig. 1 show the existence of MgO in the samples. MgO is mainly present in the grain boundary as an insulating phase, which reduces the effective cross-sectional area of the samples and then increases the resistivity. The effective cross-sectional area ($A_F$) can be estimated by the equation, $A_F = \Delta \rho_{\text{ideal}} / (\rho_{300 \, \text{K}} - \rho_{40 \, \text{K}})$, which was proposed by Rowell [22]. $\Delta \rho_{\text{ideal}}$ is the ideal change in resistivity from 300 K to 40 K for a fully connected sample. It is set to be 7.3 $\mu\Omega$cm according to [27]. The calculated $A_F$ is displayed in Table I. It can be found that all samples have low $A_F$s, indicating poor connection in the samples.

Sample B has larger $A_F$ than sample A. This may be due to the improved crystallinity and disappearance of MgB$_2$ with increased sintering time. However, $A_F$ in sample C is smaller than sample B. The reason can be attributed to larger amount of MgO in sample C, which obstructs the flow of the current and increases the resistivity.

From the resistivity curves under different magnetic fields, the irreversibility field ($H_{\text{irr}}$) and the upper critical field ($H_{c2}$), can be derived, using the 10% and 90% of the normal state resistivity. The results are shown in Fig. 3. It can be seen that $H_{c2}$ has the concave temperature-dependence curves. It is evident that $H_{c2}$ and $H_{\text{irr}}$ in the limited field regime measured increase with the sintering time. $H_{c2}$ and $H_{\text{irr}}$ at $T/T_c = 0.7$ for the three samples have been collected from Fig. 3 and plotted against microstrain in the inset of Fig. 3. It is clear that both $H_{c2}$ and $H_{\text{irr}}$ linearly increase with microstrain. The low microstrain indicates less lattice distortion inside the MgB$_2$ grains and then larger mean free path ($l$) of the superconducting electrons.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering time</th>
<th>MgO (%)</th>
<th>MgB$_2$ (%)</th>
<th>Lattice parameters</th>
<th>Parameters for the Three Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10 min</td>
<td>4.75</td>
<td>5.82</td>
<td>3.083 3.524</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>30 min</td>
<td>6.44</td>
<td>5.82</td>
<td>3.082 3.522</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3 h</td>
<td>8.5</td>
<td>5.82</td>
<td>3.085 3.526</td>
<td></td>
</tr>
</tbody>
</table>

Table I: Parameters for the three samples.
significant improvement under high fields at both 5 K and 20 K. Sample B exhibits the highest $J_c$ of $\sim 6722 \text{ Acm}^{-2}$ at 5 K and 8 T, which is more than five times higher than that of sample A and almost 2 times higher than that of sample C. The $J_c$ values at 20 K and 4.87 T follow the same trend, namely 360 Acm$^{-2}$, 2450 Acm$^{-2}$ and 1840 Acm$^{-2}$ for sample A, B and C, respectively. It has been known that the grain boundary pinning is the major pinning mechanism at high fields in MgB$_2$. The $J_c$ caused by the surface pinning can be calculated by $\mu_0 S_\gamma (H/2)^2/(4\pi^2 H^{1/2} H_c^{1/2})$ [28], where $S_\gamma$ is the grain boundary surface area per unit volume, $H_c$ is the upper critical field, $\kappa$ is the Ginzburg-Landau parameter and $H$ is the applied field. It can be concluded from this equation that $J_c$ at high fields near $H_c$ is dominantly determined by $H_c$ and $S_\gamma$ [29]. In addition, the connectivity ($A_F$) also affects $J_c$. Fig. 5 shows field emission gun scanning electron microscopy (FEG-SEM) images of samples A, B and C. It can be seen that the grain size has no significant change among samples. Therefore, the $J_c$ difference is not caused by the change of $S_\gamma$. We calculate a parameter $\alpha = A_F H_c S_\gamma$, which combines two major factors ($A_F$ and $H_c$) influencing $J_c$ and plot $\alpha$ against $J_c$'s at 20 K and 4.87 T for three samples in the inset of Fig. 4. Fig. 3 could not give the $H_c$ values at 20 K. $H_c$ at 22.5 K is roughly used to replace $H_c$ at 20 K. This figure produces a very good linear relationship between $\alpha$ and $J_c$. It clearly indicates that the improved $J_c$ is mainly caused by the improved connectivity and the increased $H_c$.

IV. CONCLUSION

MgB$_2$ samples were prepared by in situ reaction method and sintered in flowing welding grade Ar. The effect of the sintering time on superconductivity of MgB$_2$ has been investigated. The sintering time changes by 10 minutes, 30 minutes and 3 hours. It has been found that the amount of MgO increases with the sintering time and the sample with 30 minutes sintering time has the smallest lattice parameters. $H_c$ and $H_{int}$ increase with the sintering time and they have linear relationships with microstrain. The sample sintered for 30 min exhibits the highest $J_c$ at high fields. The reason can be attributed to the improved connectivity and the increased $H_c$.

ACKNOWLEDGMENT

The author would like to thank Dr. T. Silver for helpful discussions, Dr. J. Horvat for his help with measurements, the Australian Research Council, Hyper Tech Research Inc. and CMS Alphatech International Ltd for financial support.

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