SiC and Carbon Nanotube Distinctive Effects on the Superconducting Properties of Bulk MgB2

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SiC and carbon nanotube distinctive effects on the superconducting properties of bulk MgB$_2$

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(Received 15 September 2007; accepted 23 November 2007; published online 22 January 2008)

This work describes in detail the simultaneous enhancement of the upper critical field ($H_{c2}$) and the critical current density ($J_c$) of MgB$_2$ bulk samples doped with nano-SiC particles, as well as single-walled and double-walled (dw) carbon nanotubes (CNTs). The magnetization properties were examined in a superconducting quantum interference device magnetometer, and four-probe transport measurements were performed using a 50 T pulsed magnet to determine $H_{c2}(T)$. We found that the $J_c$ enhancement is similar in all doped samples at 5 K but nano-SiC addition is more effective to improve the flux pinning in the high temperature range ($T > 20$ K); this improvement cannot solely be attributed to the C incorporation to the lattice but also to the presence of other types of defects (i.e., several kinds of nanoinclusions). CNTs produce a better C incorporation that is more effective to enhance $H_{c2}$ [i.e., dwCNT-doped samples reached a record $H_{c2}(0) \sim 44$ T value for bulk MgB$_2$]. All the $H_{c2}(T)$ curves obtained for different types of doping can be successfully described using a model for a two-gap superconductor in the dirty limit. © 2008 American Institute of Physics. [DOI: 10.1063/1.2832463]

I. INTRODUCTION

Technological applications of MgB$_2$ superconductor are directly linked to the enhancement of its critical current density ($J_c$) and the upper critical field ($H_{c2}$). The pinning force may be improved by the incorporation of defects (nanoparticle doping, chemical substitutions, etc.). On the other hand, the doping level affects the interband scattering coefficients $\Gamma_{\alpha\beta}$, $\Gamma_{\alpha\alpha}$ and the diffusivity of each band $D_{\alpha\alpha}$, $D_{\alpha\beta}$ as predicted by Gurevich et al., and these changes may cause a significant $H_{c2}$ variation. Earlier attempts succeeded in raising the intragrain $J_c$ through the incorporation of Mg$_2$(B$_1$-$x$O$_x$)$_2$, SiC, Al, Dy$_2$O$_3$, nano-C, and carbon nanotubes which produce a decrease in the critical temperature ($T_c$) by chemical substitution and probably lattice strain. The improvement of intergrain $J_c$ in bulk samples is related to grain connectivity and may be achieved by optimizing the processing parameters (i.e., ultrasonication, HIPing, applying magnetic field during the sintering process, etc.). The best results for $H_{c2}(0)$ and $J_c$ at high field ($H > 5$ T) and 4 K in polycrystalline samples were achieved using C and SiC, respectively. Although the effect of carbon substitution is one of the most studied in MgB$_2$, the results on C solubility and the effect of C doping on $T_c$, $J_c$, and $H_{c2}$ reported so far vary significantly, due to precursor materials, fabrication techniques, and processing conditions used. Recently, Matsumoto et al. reported that $J_c$ in SiC-alloyed MgB$_2$ tapes depends on a complex relation between grain connectivity, $H_{c2}$, and flux pinning induced by grain boundaries and precipitates. However, the distinct effect of C incorporation through different routes in $J_c$ and $H_{c2}$ is still not entirely understood.

The purpose of this work is to understand the role of C substitution and other defects on $J_c$ and $H_{c2}$ of bulk MgB$_2$ by studying samples doped with optimum content of SiC, single-walled (sw), and double-walled (dw) carbon nanotubes (CNTs). We found that all these additions simultaneously produce the enhancement of $J_c$ and $H_{c2}$. The enhancement of $J_c$ is similar at low temperatures in all three samples, but nano-SiC-doped sample has higher $J_c$ at 20 K, indicating that the pinning is stronger in this sample due to the presence of other types of defects (i.e., Mg$_2$Si and other nonsuperconducting nano-inclusions). Record values of $H_{c2}(4$ K$)=41.9$ T [with extrapolated $H_{c2}(0) \sim 44$ T] are reached for dwCNT addition that correspond to the highest C-substitution level achieved.

II. EXPERIMENTAL

Nano-SiC-doped samples were prepared using a reaction in situ technique. Magnesium (–325 mesh, 99%) and amor-
phous boron (99%) were mixed with commercial 10 wt% SiC (20 nm). The mixed powders were uniaxially pressed into pellets of 10 mm in diameter and 2 mm in thickness, sealed in an Fe tube and then heated at temperatures 700 °C for 1 h in flowing high purity Ar. This was followed by furnace cooling to room temperature. Undoped and CNT-doped MgB$_2$ samples were also prepared by solid-state reaction with 0 and 10 at. % nominal C contents, respectively, with similar starting materials, and single-walled (diameter of 1.1 nm, length of 0.5–100 μm, Aldrich) or double-walled carbon nanotubes (diameter of 1.3–5 nm, length of ≈50 μm, 90% Aldrich) as the source of carbon. The powders were grinded under nitrogen atmosphere inside a glovebox and pressed under ~500 MPa into small pellets with dimensions of 6 mm in diameter and ∼4 mm in thickness, wrapped together with extra 20 at. % Mg turnings (99.98% Puratronic) in Ta foil and then placed in an alumina crucible inside a tube furnace in flowing Ar/H$_2$ at 900 °C for 30 min. The synthesis temperatures were the optimal ones for each kind of doping.5,11

In both cases (SiC and CNT) part of carbon dissolves into the MgB$_2$ structure during the fabrication process,13,19 and the shift in the $a$-lattice parameter, obtained from x-ray diffraction, can be used as a measure of the actual amount of C ($x$) in the MgB$_{1-x}$C$_x$$_2$ structure.22 The synthesis temperature, lattice parameters, and $x$ values obtained from fitting the single crystal data of Kazakov et al.25 and the neutron diffraction data of Avdeev et al.27 are listed in Table I.

### III. RESULTS AND DISCUSSION

Figure 1 shows the normalized dc magnetization as a function of temperature ($T$), measured with a Quantum Design® superconducting quantum interference design magnetometer, in a field of 20 Oe using a zero field cooling process. The $\Delta T_c$ (90%–10%) of the superconducting transitions are lower than 1 K in all cases (except in sample with swCNT $\Delta T_c \sim 2$ K) indicating a homogeneous distribution of the C incorporated into the lattice. The inset displays the correlation between $T_c$ and $x$ for all samples listed in Table I. We observe the same dependence reported in previous works.22,25,28

The $H_{c2}(T)$ dependence was obtained from four-probe transport measurements in a 200 ms midpulse magnet up to 50 T at NHMFL-LANL, performed at temperatures between 1.4 and 35 K. Figure 2(a) displays the $H_{c2}$ defined as the onset (extrapolation of maximum slope up to normal state resistivity) of the $R$ versus $H$ as a function of the reduced temperature $t=T/T_{c0}$, where $T_{c0}=39$ K (Ref. 29) for all samples, as listed in Table II. The lines are fits to the data with the model proposed by Gurevich.7 The fitting parameters in the model are the intraband electron diffusivities $D_{\sigma}$ and $D_{\pi}$, and the interband scattering rates $\Gamma_{\pi\sigma}$ and $\Gamma_{\sigma\pi}$. We optimized the diffusivity ratio $\eta=D_{\sigma}/D_{\pi}$ and interband scattering parameter $g=(\Gamma_{\pi\sigma}+\Gamma_{\sigma\pi})/\sqrt{2\pi k_B T_{c0}}$ to fit the measurements using Eq. (1) from Ref. 8 as described elsewhere.11

The upward curvature, characteristic of the presence of two gaps,10 is apparent in these $H_{c2}(T)$ data. The inset displays the $H_{c2}(0)$ extrapolations and the fit parameters $1/D_{\pi}$, $1/D_{\sigma}$ as function of $x$. We observe that $H_{c2}(0)$ increases with $x$ and has a good correlation with the fit parameter behavior. This enhancement is the result of changes in the diffusivity coefficients, as a consequence of C incorporation in the B site, affecting not only the $\sigma$ band but also the $\pi$ band. Changes in the interband scattering coefficient are also reflected in $T_c$ decrease.8

The CNT additions produce a larger C incorporation than SiC, probably of the higher synthesis temperature, resulting in samples with lower $T_c$. The dwCNT sample has the highest C content into the lattice, indicating that using this kind of inclusions is an easier way to incorporate C. This allows to reach a record $H_{c2}$ value for this sample. Earlier MgB$_2$ carbon doped data from Wilke et al.22,23 also indicate an initial rapid rise for lower C contents that then slows down, reaches a maximum at intermediate carbon concentrations, and decreases for larger C contents and the same behavior was reported for MgB$_2$ single crystals.30 The $H_{c2}(0)$ of dwCNT is close to the maximum $H_{c2}$ value as a function of $x$.11 A decrease in $H_{c2}(0)$ was also observed for a larger $x$.
value [see Fig. 2(b)], in agreement with very recently reported data. Matsumoto et al. reported a similar to our record \( H_{c2}(0) \) value for a SiC-doped MgB\(_2\) tape prepared by the powder-in-tube (PIT) method. These results correspond to a PIT tape sample that probably has some texturing and the reported \( H_{c2} \) data were measured with the applied field parallel to the tape. Since we measured randomly oriented polycrystalline bulk samples, our results cannot be easily compared with those of Matsumoto et al.

The field dependences for \( J_c \), calculated from magnetization using the Bean model, at 5 and 20 K are illustrated in Fig. 3(a). The \( J_c \) enhancement indicates that both CNT and SiC increase the amount of pinning centers with respect to the undoped sample. This improvement comes part from C\(_d\) doping, and part may come from an improvement in connectivity and/or the pinning effect of the possible remaining CNTs, or the presence of other defects as a consequence of SiC addition, respectively. The variation between \( J_c \)'s may be due to the different defect sizes and distribution. The dwCNT sample displays a slightly higher \( J_c \) at 5 K above 5 T while the SiC's \( J_c \) is larger than the others in the whole field range at 20 K including a self-field improvement. A crude estimation of the pinning force due to small precipitates in MgB\(_2\) indicates that the smaller the size, the higher must be the density of those defects to be effective. In particular, if we consider the di-

### TABLE II. Reduced temperature \( t=T/T_{c0} \) residual resistivity ratio (RRR) = \( \rho(295 \text{ K})/\rho(40 \text{ K}) \), and parameters \( D_x \) and \( D_e \) obtained by fitting \( H_{c2}(T) \) curves with Eq. (1) of Ref. 11 (for complete explanation see Refs. 7 and 8).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( t )</th>
<th>( D_x )</th>
<th>( D_e )</th>
<th>( -H_{c2}(0) ) (T)</th>
<th>RRR</th>
<th>( \rho(40 \text{ K}) ) (( \mu \Omega \text{ cm} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>0.987</td>
<td>0.56 \times 10^{-4}</td>
<td>1 \times 10^{-5}</td>
<td>17.7</td>
<td>2.2</td>
<td>90</td>
</tr>
<tr>
<td>SiC</td>
<td>0.945</td>
<td>0.29 \times 10^{-4}</td>
<td>4.328 \times 10^{-6}</td>
<td>35.2</td>
<td>1.74</td>
<td>300 \footnote{Reference 13}</td>
</tr>
<tr>
<td>swCNT</td>
<td>0.923</td>
<td>0.357 \times 10^{-4}</td>
<td>3.838 \times 10^{-6}</td>
<td>33.5</td>
<td>1.41</td>
<td>91</td>
</tr>
<tr>
<td>dwCNT</td>
<td>0.854</td>
<td>0.229 \times 10^{-4}</td>
<td>2.772 \times 10^{-6}</td>
<td>44.4</td>
<td>1.38</td>
<td>&lt;80</td>
</tr>
</tbody>
</table>

SiC increase the amount of pinning centers with respect to the undoped sample. This improvement comes part from C\(_d\) doping, and part may come from an improvement in connectivity and/or the pinning effect of the possible remaining CNTs, or the presence of other defects as a consequence of SiC addition, respectively. The variation between \( J_c \)'s may be due to the different defect sizes and distribution (swCNT, dwCNT, and SiC). The dwCNT sample displays a slightly higher \( J_c \) at 5 K above 5 T while the SiC's \( J_c \) is larger than the others in the whole field range at 20 K including a \( J_c \) self-field improvement. A crude estimation of the pinning force due to small precipitates in MgB\(_2\) indicates that the smaller the size, the higher must be the density of those defects to be effective. In particular, if we consider the di-

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**FIG. 2.** Upper critical field \( H_{c2}(0) \) vs \( t=T/T_{c0} \) from transport experiments (symbols), where \( T_{c0}=39 \) K (Ref. 29) and \( H_{c2} \) was defined at the onset of the \( R(H) \) curves for all samples. Dashed lines correspond to fits using Eq. (1) in Ref. 11. The inset shows the dependence of \( H_{c2} \) extrapolated to 0 K, normalized \( 1/D_x \) and \( 1/D_e \) with \( x \) (dotted lines are guides to the eyes).

**FIG. 3.** (a) \( J_c \) field dependence obtained from magnetization loops for all samples described in Table I at 5 K (solid symbols) and 20 K (open symbols). (b) \( F_p \) as a function of the applied field of all four samples at 20 K. The inset shows the same normalized \( F_p \) as a function of the reduced field where the criterion for \( h^* \) is \( J_c=100 \text{ A/cm}^2 \). The full line is the theoretical field dependence of \( F_p/F_p^{\text{max}} \) proposed for the grain boundary flux pinning.
The normalized $F_p$'s are slightly higher than the expected for grain boundary flux pinning, which indicates that the CNT additions resulted in an additional pinning. This extra pinning effect and the better grain connectivity are not so effective due to a $T_c$ decrease (see Table I). In contrast, SiC sample presents a very low connectivity, so the improved in-field $J_c$ is due to a stronger pinning. Several potential pinning centers were introduced by SiC doping shown secondary phases in Fig. 4, including MgSi$_2$, BC, BO$_x$, SiBO$_x$, and unreacted SiC as identified by electron-energy-loss spectroscopy and x-ray diffraction, which are all at a scale below 10~nm, and provide effective pinning at all the temperatures up to $T_c$.

The improvement in $J_c$ is not linearly related to $x$, and it is not clear whether C incorporation, or the remaining intra-or intergrain defects, is the predominant effect. It is worthy to note that SiC may produce the best pinning effect owing to the following factors: C substitution induced embedded defects within grains and a strong grain boundary pinning due to low processing temperature. Nanoscale SiC can react with Mg at temperatures as low as 600 °C at which MgB$_2$ formation takes place. The free C released from the reaction can be easily incorporated into the lattice while the nanoscale impurities such as Mg$_2$Si are included in the grains as nano-inclusions. Low temperature processing produces small grains and unreacted impurities with a high density of nanoscale defects, which act as effective pinning centers. In contrast, C substitution for B in CNT-doped samples was only achieved at higher temperatures (900 °C). Thus, flux pinning in CNT-doped samples is not as strong as in SiC-doped samples at high temperatures apparently due to a decrease in $T_c$ and a low density of defects.

IV. SUMMARY

In summary, we found that additions of SiC or CNT produce simultaneous enhancement of $J_c$ and $H_{c2}$, but there is a clear difference in the origin of flux pinning effects in both cases. Nano-SiC is more effective to improve the flux pinning at high temperatures (i.e., 20 K), and this improvement cannot be solely attributed to the C incorporation to the lattice but to the presence of high density of defects including grain boundaries and also other nanoprecipitates. On the contrary, CNTs produce a better C incorporation that is more effective to enhance $H_{c2}$, reaching a record $H_{c2}(0)$ value for bulk dwCNT MgB$_2$, but the enhancement of $J_c$, which is very good at 5 K, is not as good as SiC at 20 K. Finally, the measured $H_{c2}(T)$ in all samples are successfully described using a theoretical model for a two-gap superconductor in the dirty limit, and corroborates that the C incorporation to the lattice is correlated with the $\pi$-band scattering.

ACKNOWLEDGMENTS

This work was supported at Centro Atómico Bariloche by CONICET, Fundación Antorchas, and SECyT-PICT; at Los Alamos National Laboratory by the Office of Electricity Delivery and Energy Reliability, US Department of Energy; at Wollongong by Australian Research Council and Hyper
Tech Research Inc.; and at the NHMFL by the US National Science Foundation, the State of Florida, and the US Department of Energy.


29In Refs. 7 and 11 is defined $T_{c_{o}}=T_{c}(g=0)$ with $g$ the interband scattering parameter. This value corresponds to the clean limit MgB$_2$ sample.


