2007

Effect of processing temperature on high field critical current density and upper critical field of nanocarbon doped MgB2

W.K. Yeoh  
*University of Wollongong*

J. Horvat  
*University of Wollongong, jhorvat@uow.edu.au*

J. H. Kim  
*University of Wollongong, jhk@uow.edu.au*

X. Xu  
*University of Wollongong*

S. X. Dou  
*University of Wollongong, shi@uow.edu.au*


**Publication Details**

Effect of processing temperature on high field critical current density and upper critical field of nanocarbon doped MgB$_2$

W. K. Yeoh,$^{a}$ J. Horvat, J. H. Kim, X. Xu, and S. X. Dou

Institute for Superconducting and Electronic Materials, University of Wollongong, Northfields Avenue, Wollongong, New South Wales 2522, Australia

(Received 4 December 2006; accepted 14 February 2007; published online 20 March 2007)

Correlation of upper critical field ($H_c2$) and critical current density ($J_c$) with processing temperature of nano-C doped MgB$_2$ has been studied in comparison to SiC and pure MgB$_2$. SiC and C doped MgB$_2$ exhibit opposite trends in the dependence of $J_c$ and $H_c2$ on sintering temperature. This is explained by different reactivities of carbon available upon creation of MgB$_2$ for the two types of doping. Nanocarbon doped MgB$_2$ requires sintering temperatures in excess of 900 °C to obtain high boron substitution for carbon, enhancing the vortex pinning and impurity scattering of charge carriers. However, carbon substitution in nano-SiC doped MgB$_2$ occurs at less than 650 °C, allowing lower sintering temperature and high degree of carbon substitution. Both pure and SiC doped MgB$_2$ benefit from low sintering temperature, which results in more grain boundary defects. Substantial carbon substitution can compensate for the disadvantage of sintering at high temperature of nano-C doped MgB$_2$, giving the best $J_c$ of 4.8×10$^3$ A/cm$^2$ at 4.5 K and 12 T. This is comparable to the low-temperature sintered nano-SiC doped MgB$_2$ wires. © 2007 American Institute of Physics.

There have been several demonstrations of enhanced vortex pinning and critical current density, $J_c$, in the MgB$_2$ superconductor by doping, which produced partial substitution of boron for carbon, including SiC, B$_4$C, Carbon nanotube, and nano-C doping.$^{1-5}$ Substitution of C in the B site also significantly increases the upper critical field, $H_c2$.6-9

Despite numerous reports on carbon substitution,10-14 no optimization of the processing temperature has been reported yet. In this work, we demonstrate that nano-C doping can be one of the most promising procedures, besides nano-SiC doping, for the enhancement of flux pinning in MgB$_2$ at high magnetic fields. We show that the mechanisms of carbon substitution for nano-C doped MgB$_2$ are different than for optimized nano-SiC doped MgB$_2$.

Explanation of our results is based on the dual reaction model,$^{15}$ where fresh C can be easily released from SiC and incorporated into the B site of MgB$_2$ at low temperature (=600 °C), resulting in impurity scattering of charge carriers and vortex pinning. Matsumoto et al. reported that enhanced grain connectivity degraded $H_c2$ and flux pinning for nano-SiC doped MgB$_2$ sintered at high temperature.16 Moreover, carbon doped MgB$_2$ has an improved homogeneity at higher processing temperature, as compared to SiC doping.17

Monofilamentary wires of nominal atomic ratio MgB$_2$ and MgB$_{1.9}$C$_{0.1}$ (carbon doped samples) were prepared by powder in tube via in situ reaction method, with powders of magnesium (99%, −325 mesh), amorphous boron (99%, 1–2 μm), and amorphous carbon (<20 nm). All the concentrations given here are the nominal values. The mixture was packed into Fe tubes 140 mm long, with an outer diameter of 10 mm and inner diameter of 8 mm, which were subsequently drawn to a wire of 1.4 mm in diameter. The details have been described elsewhere.18 All samples were sealed in Fe tubes or Zr foil, heated with 5 °C/min in flowing high purity Ar from 650 to 950 °C for 30 min, and furnace cooled to room temperature.

The transport critical current, $I_c$, at 4.2 K was measured by the four-probe method with a criterion of 1 μV/cm. The $I_c$ was obtained by dividing the $I_c$ with the cross-sectional area of superconducting core. $T_c$ was obtained from intersections of linear extrapolations of ac susceptibility versus temperature plots below and above the superconducting transition temperature. Resistivity in field was measured by the four-probe method in Physical Property Measurement System and $H_c2$ was determined at the 10% of the value of normal state resistivity at 40 K. The grain morphology and microstructure were examined by scanning electron microscopy (SEM). Lattice parameter $a$ was obtained by using the unit cell software for XRD analysis. Effective current-carrying area fraction ($A_F$) was obtained by using the analysis developed by Rowell,19,20 where $A_F$=(ρideal−ρ(40 K)) and $Δρ_{ideal}$=7.3 μΩ cm.21 The average density was calculated by dividing the mass of the sample by its volume.

![FIG. 1. Dependence of $J_c$ at 4.2 K and 12 T on sintering temperature for nano-SiC and nano-C doped wires, as well as pure MgB$_2$ wire.](image-url)
Figure 1 shows the dependence of transport $J_c$ at 4.2 K and 12 T on sintering temperature, for undoped, nano-SiC, and nano-C doped samples. Both pure and nano-SiC doped MgB$_2$ have the best $J_c$ for low sintering temperature, with the highest value of around $7 \times 10^6$ A/cm$^2$ obtained for nano-SiC doped MgB$_2$ sintered at 650 °C. The value of $J_c$ decreases gradually with increasing the sintering temperature for SiC doped and undoped samples. On the other hand, the $J_c$ of nano-C doped samples improves systematically as the sintering temperature increases from 650 to 950 °C, with the best $J_c$ of 4.8 $\times 10^7$ A/cm$^2$ at 12 T for samples sintered at 950 °C. Similar variation was obtained for all other fields between 8 and 12 T. We note that an Fe$_2$B interface layer may occur in MgB$_2$/Fe wires. However, there was no observable interface layer in any of our samples, presumably due to shorter sintering time and different boron powder than in Refs. 13, 23, and 24. Further, the transport $J_c$ in the present work is in qualitative agreement with the magnetic $J_c$ of bulk samples prepared in the same way, but without iron sheath. Thus, any effects, due to a possible undetected interface layer and depletion of boron, do not play a role in this discussion.

The variation of $J_c$ (H=12T) with the sintering temperature (Fig. 1) strongly suggests that processing temperature affects $J_c$ because of the following: enhancement of grain boundary pinning by growing small crystals (low-temperature sintering) or introduction of defects/dislocations by carbon substitution (nano-SiC and nano-C doping). As opposed to nano-C doping, nano-SiC doping does not require high-temperature sintering to obtain substitution of boron for carbon.

$H_{c2}$ followed the same trend as $J_c$: the $H_{c2}$ for nano-C doped MgB$_2$ increased with sintering temperature, while for undoped and SiC doped samples it followed the opposite trend (Fig. 2). The residual resistivity ratio (RRR) is derived as $R$(300 K)/$R$(40 K) and for nano-C doped samples it decreases with the sintering temperature (Table I). However, for the undoped and SiC doped MgB$_2$, it follows the opposite trend. All of this can be understood in terms of carbon substitution being the dominant defect changing the $H_{c2}$ for nanocarbon doped samples and hence increasing the charge carrier scattering rates. On the other hand, the drop of $H_{c2}$ and higher RRR for both undoped and SiC doped MgB$_2$ sintered at high temperature suggests a reduction of the impurity scattering of charge carriers due to improved crystallinity with high sintering temperature. Impurity scattering of charge carriers in nano-SiC doped MgB$_2$ is contributed by both C substitution and large crystal disorder due to crystal growth at low temperature and small crystal size. The latter is annealed out at higher temperatures, thus decreasing the scattering of charge carriers.

Further, resistivity decreases with sintering temperature (Table I). Resistivity of carbon doped MgB$_2$ was reported to increase with the amount of carbon added to the sample. This high resistivity may be due to the presence of unreacted carbon between the grain boundaries. The drop of the normal state resistivity with sintering temperature in the present work can be ascribed to an enhancement of $A_F$, where the $A_F$ value increases from 0.15 to 0.22 as the sintering temperature increases from 700 to 900 °C (Table I). Moreover, SEM images (Fig. 3) for 5 at. % nanocarbon doped MgB$_2$ display well-consolidated and better connected grains and denser core (Table I) with the increase of sintering temperature from 700 to 900 °C, due to a better and more homogeneous reaction. Boron substitution for carbon is more effective at high temperatures, which reduces the amount of unreacted carbon between crystals, increasing the value of $A_F$ and reducing RRR.

The improvement of $J_c$ at high field can be achieved by enhancement of $H_{c2}$ due to the charge carrier scattering by grain boundaries and C substitution. SiC provides moderate amounts of carbon substitution, largely independent of sintering temperature. Low processing temperature results in small grain size, increasing grain boundary scattering, and

![FIG. 2. $H_{c2}$ vs $T/T_c$ for undoped, SiC doped, and C doped MgB$_2$ wires sintered at various temperatures.](Image)

![FIG. 3. Microstructure analysis for the carbon-substituted MgB$_2$ sintered at 700 and 900 °C for (a) and (b), respectively.](Image)
consequently $H_c$ and $J_c$. For this reason, high-temperature sintering is counterproductive for both pure and SiC doped MgB$_2$ because this only increases the grain size, whereas carbon can be substituted into MgB$_2$ for nano-SiC doped samples at low temperatures (650 °C).

Even though carbon doped samples have a large grain size for high sintering temperature (Fig. 3), similar to pure and SiC doped samples, the $H_c$ and $J_c$ of nanocarbon doped MgB$_2$ are significantly improved due to strong charge carrier scattering effect and vortex pinning caused by carbon substitution. Substantial carbon substitution can compensate the disadvantage of sintering at high temperature for the nano-C doped MgB$_2$, giving the values of $J_c$ at high fields comparable to nano-SiC doped MgB$_2$.

In conclusion, we have shown that the major enhancement of $H_c$ and $J_c$ for nano-C and SiC doped MgB$_2$ has a different origin, although both share carbon substitution as an important factor. Pure and SiC doped MgB$_2$ are best when sintered at low temperature, resulting in strong grain boundary defects. Carbon substitution of nano-SiC doped MgB$_2$ occurs at low temperature (650 °C), giving additional advantage of charge scattering and vortex pinning by carbon. High level of carbon substitution for nano-C doping can only be achieved at high sintering temperature, at the expense of the decrease in grain boundary defects.

The author would like to thank C. H. Jiang, T. Nakane, and H. Kumakura for their help on transport $J_c$ measurement in this work. This work was supported by the Australian Research Council, Hyper Tech Research Inc., OH, Alphatech International Ltd., NZ, and the University of Wollongong. One of the authors (W.K.Y) has received an Australia-Asia Award funded by the Australian Government.