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

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Correlation of upper critical field (H_{c2}) and critical current density (J_c) with processing temperature of nano-C doped MgB₂ has been studied in comparison to SiC and pure MgB₂. SiC and C doped MgB₂ 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 MgB₂ for the two types of doping. Nanocarbon doped MgB₂ 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 MgB₂ occurs at less than 650 °C, allowing lower sintering temperature and high degree of carbon substitution. Both pure and SiC doped MgB₂ 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 MgB₂, giving the best J_c of 4.8×10^3 A/cm² at 4.5 K and 12 T. This is comparable to the low-temperature sintered nano-SiC doped MgB₂ wires. © 2007 American Institute of Physics. [DOI: 10.1063/1.2715026]

There have been several demonstrations of enhanced vortex pinning and critical current density, J_c , in the MgB₂ superconductor by doping, which produced partial substitution of boron for carbon, including SiC, B₄C, 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 MgB₂ at high magnetic fields. We show that the mechanisms of carbon substitution for nano-C doped MgB₂ are different than for optimized nano-SiC doped MgB₂.

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 MgB₂ 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 MgB₂ sintered at high temperature.¹⁶ Moreover, carbon doped MgB₂ has an improved homogeneity at higher processing temperature, as compared to SiC doping.¹⁷

Monofilamentary wires of nominal atomic ratio MgB₂ 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%, $1-2$ μ m), 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 μ V/cm. The J_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 $A_F = \Delta\rho_{\text{ideal}} / [\rho(300 \text{ K}) - \rho(40 \text{ K})]$ and $\Delta\rho_{\text{ideal}} = 7.3$ $\mu\Omega$ 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 MgB₂ wire.

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FIG. 2. H_{c2} vs T/T_c for undoped, SiC doped, and C doped MgB_2 wires sintered at various temperatures.

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 $7 \times 10^3 \text{ A/cm}^2$ obtained for nano-SiC doped MgB_2 sintered at 650 °C.²² 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 at 4.2 K of $4.8 \times 10^3 \text{ A/cm}^2$ 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_2B interface layer may occur in MgB_2/Fe wires.^{13,23,24} 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,⁵ 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 $J_c(H=12 \text{ T})$ 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

FIG. 3. Microstructure analysis for the carbon-substituted MgB_2 sintered at 700 and 900 °C for (a) and (b), respectively.

trend (Fig. 2).^{25,26} The residual resistivity ratio (RRR) is derived as $R(300 \text{ K})/R(40 \text{ K})$ 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.^{16,26} 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.^{27–29} 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.^{30–32} 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 ,¹⁹ 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.^{33,34} SiC provides moderate amounts of carbon substitution, largely independent of sintering temperature.¹⁵ Low processing temperature results in small grain size, increasing grain boundary scattering, and

TABLE I. Superconducting properties as a function of reaction temperature for nanocarbon doped MgB_2 samples with nominal composition as $\text{MgB}_{1.9}\text{C}_{0.1}$.

Processing condition (°C)	T_c (K)	a lattice parameter (Å)	$\text{MgB}_{2-x}\text{C}_x$, actual x	$\rho(40 \text{ K})$ ($\mu\Omega \text{ cm}$)	$\rho(300 \text{ K})$ ($\mu\Omega \text{ cm}$)	A_F	RRR	Average density (g/cm^3)
700	36.25	3.0841(1)	0.021	67	114	0.15	1.70	1.235
900	35.96	3.0796(6)	0.049	58	98	0.18	1.68	1.251
1000	34.67	3.0743(4)	0.082	63	96	0.22	1.52	1.257

consequently H_{c2} and J_c .³⁴ 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).¹

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_{c2} 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_{c2} 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),¹ 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.

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