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Effect of Carbon Substitution on the Superconducting Properties of MgB2 Doped With Multi-Walled Carbon Nanotubes and Nano Carbon

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Effect of Carbon Substitution on the Superconducting Properties of MgB$_2$ Doped With Multi-Walled Carbon Nanotubes and Nano Carbon

W. K. Yeoh, J. Horvat, J. H. Kim, X. Xu, and S. X. Dou

Abstract—We have fabricated the multiwalled carbon nanotube (MWCNT) and nano-C doped MgB$_2$ bulk and wire to investigate the effect of carbon substitution in the MgB$_2$. Carbon substitution into boron site was confirmed by the shrinkage of the lattice parameter $\alpha$ with the increasing of the doping level. It was found that the lattice distortion and optimum doping level are different in the CNT and nano-C samples. This can be explained by carbon substitution, which is a more direct substitution process with the nano-C precursor. With CNT doping, carbon substitution only occurred after break out of carbon atoms from CNT. Both dopants showed significant enhancement in both magnetic critical current density, $J_c$(H), and transport critical current at high sintering temperature like 900 °C. Transport $I_c$, of magnitude 14 A and 30 A was observed at 4.2K and 12T for CNT and nano-C doping, respectively.

Index Terms—Carbon nanotube doping, critical current, magnesium diboride, nano-C doping.

I. INTRODUCTION

Aimed at substitution for boron in MgB$_2$, carbon substitution from various carbon sources is always a remarkable topic to investigate in terms of the two-band superconductivity, the critical current density and the upper critical field. In addition, the band structures and crystal structure of MgB$_2$ are similar to those of graphite. This would explicate that carbon is the most successful substitution in the boron site using various carbon sources and synthesis conditions.

The effect of C doping on the flux pinning and critical current density in MgB$_2$ using amorphous carbon [1]–[5], diamond [6], B$_4$C [7]–[9], carbon nanohorn [10] and graphite [11] have been studied, all showing improvement of $J_c$, at elevated field. The effective pinning improvement of all the samples are mainly attributed to partial C substitution despite finely dispersed small particles like MgO and MgB$_2$-C$_2$ in MgB$_2$ matrix. However, among all the carbon sources, the improvement of critical current properties of MgB$_2$ has been confirmed as most effective by doping with SiC nano powder [12]. At 20 K and 2 T, the $J_c$ for the SiC doped sample was 2.4 × 10$^5$ A/cm$^2$, which is comparable to $J_c$ values for the best Ag/Bi-2223 tapes under the same conditions.

II. EXPERIMENTAL DETAILS

Powders of magnesium (99%, ~325 mesh), amorphous boron (99%, 1–2 μm), MWCNT (>95%, outside diameter 20–30 nm, average length 0.5–200) and amorphous carbon (particle size <20 nm) with the nominal atomic ratio of MgB$_2$$_{2-x}$C$_x$ where $x = 0, 0.05, 0.1, 0.2$ and 0.3 was prepared by an in situ reaction method. MgB$_2$/Fe monofilament wires were prepared by using the powder-in-tube method. The mixture was mixed through grinding and mixed powders were packed into Fe tubes with a length of 140 mm, an outer diameter (O.D) of 10 mm, and an inner diameter (I.D) of 8 mm and subsequently drawn to wire 1.4 mm in diameter. The details have been described in [14]. All the samples were sealed in Fe tubes or Zr foil, then heat treated with a heating rate of 5 °C/min in flowing high purity Ar at 800 and 900 °C for 30 minutes, followed by a furnace cooling to room temperature.

The phase and crystal structure of all the samples were investigated using a MAC Science MX03 X-Ray diffractometer with CuKα radiation. The transport $I_c$ at 4.2 K was measured by the four-point-probe resistive method with a criterion of $1\mu$V/cm in magnetic fields up to 12 Tesla. $T_c$ was obtained from the measurements of AC susceptibility $\chi$, as a temperature at which the extrapolation of measured $(\chi',T)$ curves for $T < T_c$ and $T > T_c$ intersect. We stress that the values for $x$ are the nominal values throughout the paper, and actual substitution of C for B will be shown to be less than these values.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the (110) peak from the XRD patterns for nano C and CNT doping sintered at 900 °C for 30 min. As shown in the XRD, (110) peak shifted to the higher angle as doping level of the carbon source increased for both nano C and CNT doping. This reflects the shrinkage of the lattice parameter $\alpha$ and the lattice distortion, which is due to the partial substitution of carbon in the boron site as predicted by most of the carbon doped samples. It should be pointed out that the decrease of (110) peak in CNT samples was smaller compared to the nano
C samples. This indicates that under the same doping level and processing condition, carbon substitution is more pronounced in the nano C doped samples than the CNT samples. Since the carbon in the CNT needs to break out from the atomic carbon sheet of CNT before it can take part in the carbon substitution, the carbon substitution in the CNT consumes more energy compared to the nano C and indirectly reduces the opportunity of carbon substitution under the same conditions. Previous study showed that nanotubes tend to entangle, preventing their homogenous mixing with MgB$_2$ and dispersion [17], [20]. As a result, this will additionally suppress the reactivity of the CNT with the Mg and B powders.

Fig. 2 shows the magnetic $J_c$(H) curves at 5 K and 20 K for the nano C and CNT doped bulk samples of MgB$_{2-x}$C$_x$, where $x = 0$, 0.05, 0.1, 0.2 and 0.3 are the nominal values for C content, with all the samples sintered at 900°C for 30 min. All the $J_c$(H) curves for doped samples have a higher $J_c$ than the un-doped sample at fields above 5 T at 5 K, even for the high doping concentration like $x = 0.3$. This implies that MgB$_2$ has a high tolerance to the carbon impurities, although only partial carbon might substitute into the boron site. Nevertheless, nano C samples showed a significant variation of $J_c$, compared to the CNT doping, as the amount of carbon source increases. In fact, both groups of samples showed two different optimum doping levels under the same processing conditions, with the optimum doping level of nano C and CNT sample being $x = 0, 0.10$ and $x = 0, 0.20$, respectively. As mentioned above, the reactivity of the carbon source plays an important role to determine the carbon substitution in the MgB$_2$. The form of carbon source can substantially enhance the reactivity of the C and MgB$_2$. We believe the difference in the optimum doping levels is most likely due to the reactivity of different carbon sources which requires different kinetic energy for carbon substitution. However, the nano C doping showed a better $J_c$ performance in high field compared to the CNT sample.

Fig. 3 shows the $H_{\text{tr}}$ as a function of nominal C doping level, where $H_{\text{tr}}$ was defined as criterion of $J_c = 100$ A/cm$^2$ at 20 K. The CNT sample exhibited very slight, linear decrease of $H_{\text{tr}}$ with the doping level, while the $H_{\text{tr}}$ of the nano C sample dropped significantly more for the same doping level. The small variation of the $J_c$(H) and $H_{\text{tr}}$ may due to the poor reactivity of the CNT and hence, limited the reactivity of CNT with boron.

DTA traces of nano C and CNT doped MgB$_2$/Fe wires are shown in the Fig. 4. The pure MgB$_2$/Fe wire was included as reference. All wires were sintered at the heating rate of 5°C/min and high purity Ar gas was applied during the whole
experiment. In the pure MgB$_2$ wire, two exothermic peaks were observed at around 457 °C and 619 °C respectively. According to the Goldacker et al., the first peak is corresponding to the formation of MgO and melting of B$_2$O$_3$ due to Mg reacting with B$_2$O$_3$ to form MgO + B [23]. The second exothermic peak was a consequence of the formation of MgB$_2$ from the molten Mg and amorphous B. However, both the exothermic peaks were slightly shifted to the higher temperature for both nano C and CNT doping. This can be explained by the presence of additional impurities like nano C and CNT in the mixture of B and Mg, which delayed the reaction, compared to the pure Mg and B wire. The narrow endothermal peak around 910 °C is related to the transition of Fe sheath as reported in the [14].

Fig. 5 shows the transport critical current at 4.2 K at fields up to 12 T for MgB$_2$$_{1.0}$C$_{0.1}$ and MgB$_2$$_{1.8}$CNT$_{0.2}$ wire produced at various sintering temperatures. This composition was chosen to give the best $I_c$, based on the outcomes of previous measurements [15]. The $I_c(H)$ was improved systematically as the sintering temperature was increased from 800 °C to 900 °C, with the slope of the $I_c(H)$ becoming smaller with increasing of sintering temperature. The flux pinning in both samples was enhanced as sintering temperature increased and the best $I_c(H)$ was observed at 900 °C of sintering temperature. This result indicates that flux pinning at high sintering temperature was enhanced by a large amount of carbon substitution. The best $I_c$ was estimated to be 30 A and 14 A at 12 T and 4.2 K for nano C and CNT sample, respectively. This is in contrast with the SiC doped MgB$_2$ where low sintering temperature was the optimum temperature for the good $I_c$. The bigger $I_c$ variation shown by the nano C sample again indicated that better reactivity of C and B compared to the CNT sample.

IV. CONCLUSION

Due to carbon substitution effect, both nano C and CNT substitution exhibited excellent magnetic $I_c$ and transport $I_c$ at high temperature (900 °C). However, nano C doped MgB$_2$ resulted in better improvement of flux pinning compared to CNT doped MgB$_2$. Magnetic $I_c$ was enhanced by the factor of 1.8 at 5 K in the bulk sample, while transport $I_c$ showed an enhancement by a factor of 1.9 at 12 T and 4.2 K for nano C sample compared to CNT doped MgB$_2$. It was found that the variation in the lattice distortion, optimum doping level, magnetic $I_c$, $H_{tr}$ transport $I_c$ for CNT and nano C samples can be explained by the reactivity of carbon source. Carbon substitution is more direct process with the nano C precursor, while carbon substitution with CNT doping only occurred after break out carbon atom from CNT. However, the prospect of the CNT as means for improving the thermal stability, heat dissipation, and mechanical support of MgB$_2$ superconductor wire should also be considered.

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REFERENCES


