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Effect of Carbon Nanotube Size on Superconductivity Properties of MgB_2

W. K. Yeoh, J. Horvat, S. X. Dou, and P. Munroe

***Abstract*—Experimental results are presented for the incorporation of carbon nanotube in polycrystalline MgB_2 superconductor based on X-ray diffraction and transmission electron microscopy measurements. Electron microscopy studies show that nanotubes are embedded into the MgB_2 matrix with a fraction of nanotubes found to be unreacted and entangled. In contrast, magnetization measurements indicate a change in the critical current density with the length of nanotubes and not with their outside diameter. This implies that longer nanotubes tend to entangle, preventing their homogenous mixing with MgB_2 and dispersion. Overall, carbon nanotube doping of MgB_2 enhanced the critical density and depressed the critical temperature.**

***Index Terms*—Critical current density, MgB_2, multi-walled carbon nanotubes, nano-particle.**

I. Introduction

THE enhancement in the critical current density J_c is one of the most important challenges in superconductivity. Since the discovery of superconductivity in MgB_2 below 39 K [1], various attempts have been carried out to enhance the J_c. Although significant efforts have been carried out, it is still not clear why high J_c was obtained. Among all the techniques, doping with nano-particles is the most promising way for large-scale applications. The best result has been achieved by the nano SiC doping [2] with J_c increased by a factor of 32 at 5 K and 8 T and 14 at 30 K and 2 T, as compared to the undoped sample.

The nanoparticles have to satisfy certain criteria to be acceptable as pinning centers. Their presence should not affect the formation of superconducting phase and they should not agglomerate. By creating scattering centers for charge carriers via doping of MgB_2, it will be pushed to the dirty limit by shortening the mean free path of the charge carriers. However, this scattering will not affect the c-axis parameter with a significant shift of a-axis parameter. In the case of carbon doping, it was shown that even with the $x = 0.2$ for $MgB_{1.8-x}C_x$ the two-gap superconductivity was still observed [3].

It has been demonstrated that carbon nanotubes can be embedded in Bi-2212, thus offering a promising method for introduction of extended defects in superconductor [4]. The reasons for choosing carbon nanotubes (CNT's) are their geometrical properties and mechanical properties. The magneto-optical image investigations have revealed that CNT's are functioning like columnar defects, enhancing J_c in the Bi-based superconductor [5]. However, the flux-pinning properties were improved only at low temperatures, below 52 K [4].

In the previous studies, we studied the effect of CNT doping on the J_c and H_{c2} [6], [7]. However, it remains unclear how the size of CNT affects the J_c. We demonstrated that significant fraction of CNT can be successfully embedded in the MgB_2 matrix, as indicated by the XRD and J_c measurements. The TEM images showed that CNT's are still present after sintering at the temperature as high as 900°C. The results also indicate that further improvement of CNT doped samples can be achieved by varying the sintering temperature and sintering time. In this paper we study the effect of varying the diameter and length of CNT (Table I) on the J_c and T_c, as well as unit cell structure of the doped MgB_2.

TABLE I
OUTSIDE DIAMETER AND LENGTH OF CARBON NANOTUBES USED

Outside diameter (nm)	Average Length (μm)
< 8	0.5-200
8-15	0.5-200
20-30	0.5-2
60-100	5-15

II. Experimental Details

MgB_2 pellets were prepared by conventional solid-state reaction. High purity powders of magnesium (99%), amorphous boron (99%) and multi-walled carbon nanotubes were weighted out according to the nominal atomic ratio $MgB_{1.8}C_{0.2}$ and well mixed through grinding, then pressed into pellets of 13 mm in diameter and 1 mm thickness. The pellets were sealed in' Fe tubes, then heat treated in flowing high purity Ar at 900°C for 30 minutes, followed by a furnace cooling to room temperature. An undoped sample was also made under the same conditions for use as a reference sample. A MAC Science MX03 diffractometer with Cu K_α radiation was used to determine the crystal structure of all the samples. Si powder was used as an internal standard to calculate the lattice parameters. The magnetization was measured by a physical property measurement system (PPMS, Quantum Design). Bar shaped samples with a size of $3 \times 1.5 \times 1\ mm^3$ were cut from each pellet for magnetic measurements. J_c was calculated from the height of the magnetization loop ΔM using the critical state model. T_c was obtained

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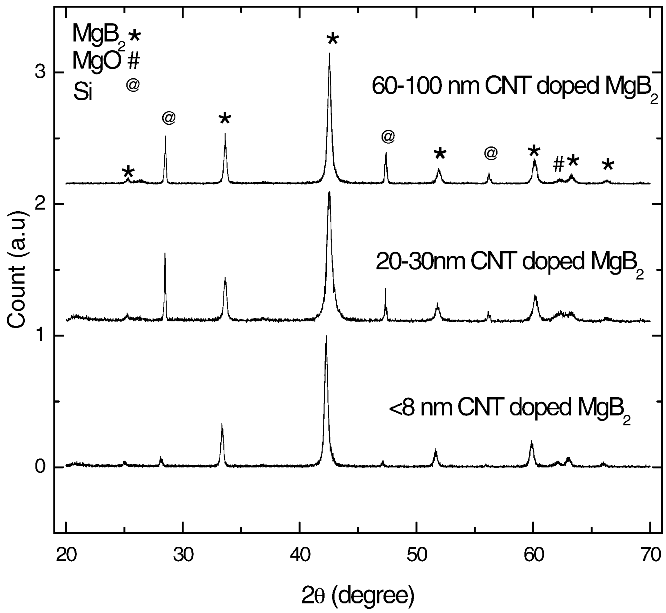

Fig. 1. X-ray diffraction pattern of different diameter size carbon nanotube that sintered in 900°C for 30 minutes.

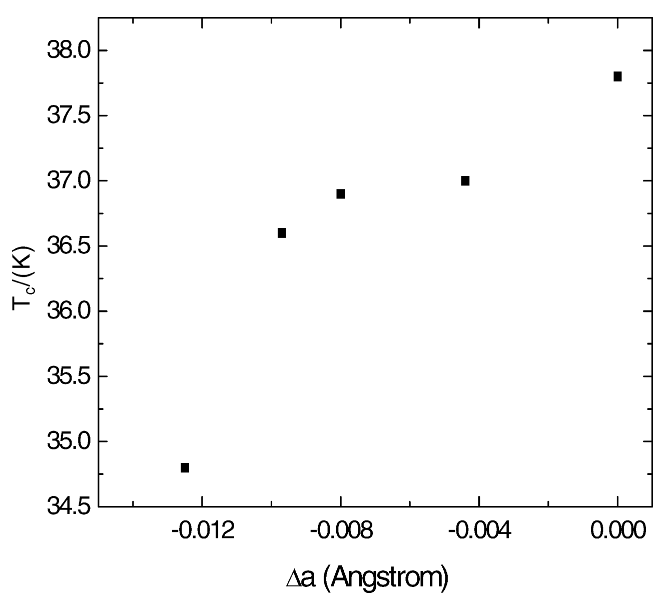

Fig. 2. Critical temperature, T_c as a function of change of lattice parameter a. Reference sample is also included as comparison.

from the measurements of AC susceptibility. The details of the experiments have been described in [6], [7].

III. Results and Discussions

The main problems we are concerned about when doping CNT into MgB_2 are the lack of chemical stability of nanotubes at elevated temperatures and reaction of nanotubes with oxygen. Sintering in the high purity argon gas environment can minimize the latter problem. The reaction of CNT with MgB_2 would be another problem since experiment showed that CNT could react quite selectively with precursor material [8].

The XRD patterns for the three samples corresponding to the different diameter of CNT's are shown in Fig. 1 with pure Si as reference. It can be seen from the XRD patterns that the major phase is MgB_2, with a minor phase of MgO, as reported in the previous studies [6], [7]. There is a shift of the (110) peaks to the higher angle that indicated a distortion of lattice parameter a although all the samples have the same nominal composition. This difference in the distortion of the MgB_2 lattice suggests that different level of substitution occurred, which may be due to the difference in CNT geometry or homogeneity of the mixing. However, the lattice parameter c remains the same.

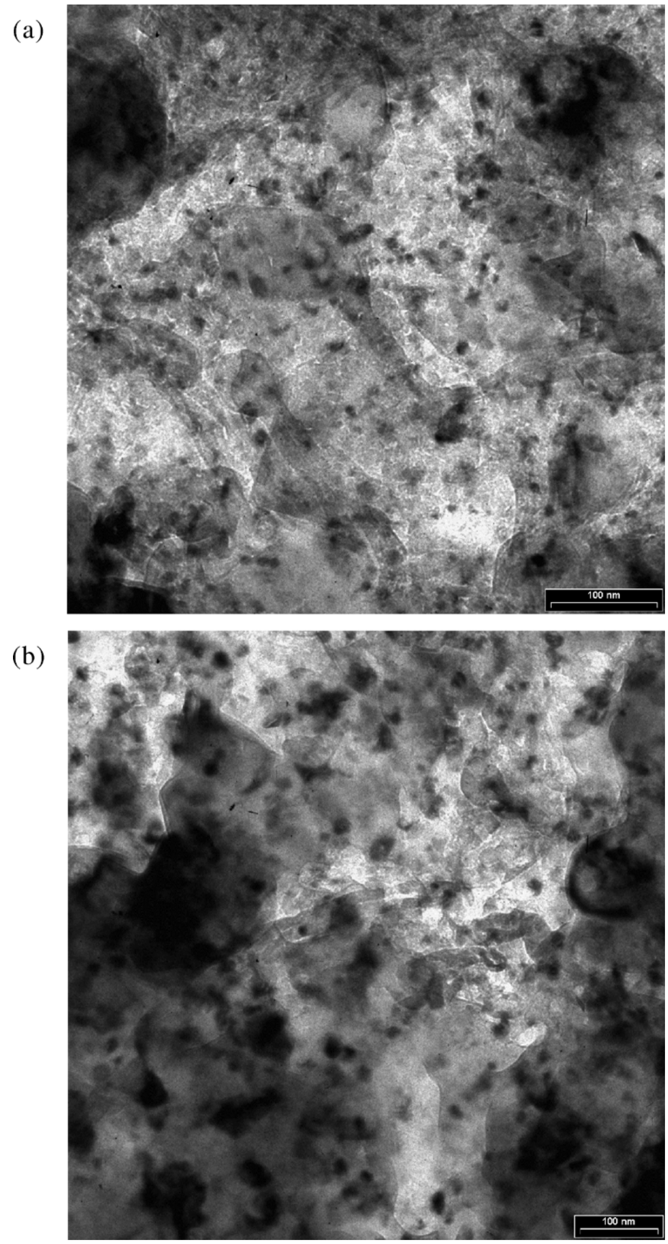

Fig. 3. TEM image showing the carbon nanotube embedded into the MgB_2 matrix for (a) carbon nanotube with diameter 8–15 nm and (b) carbon nanotube with diameter 20–30 nm.

The T_c values, shown in Fig. 2 against the shift of lattice parameter a, were defined by the onset of superconducting screening in ac susceptibility measurements. The result for pure MgB_2 is included for comparison. The 20–30 nm CNT doped MgB_2 showed the largest change in a, followed by <8 nm, 8–15 nm and 60–100 nm CNT doped MgB_2. The T_c decreased

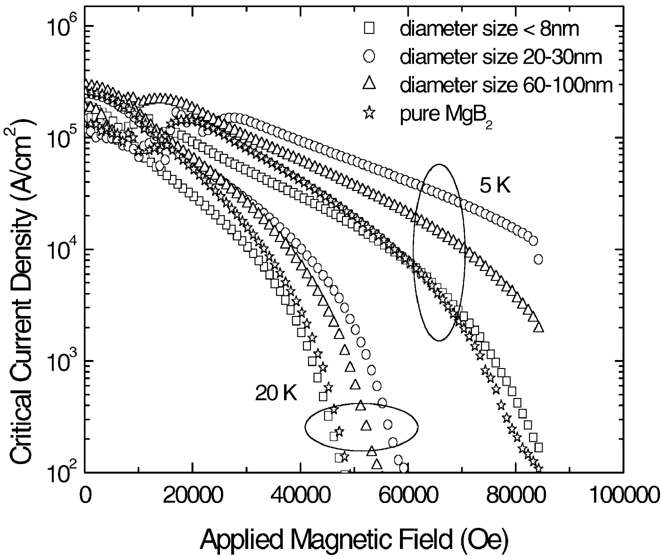

Fig. 4. A comparison of magnetic J_c (H) at 5 K and 20 K for all the carbon nanotube doped samples and the pure MgB_2.

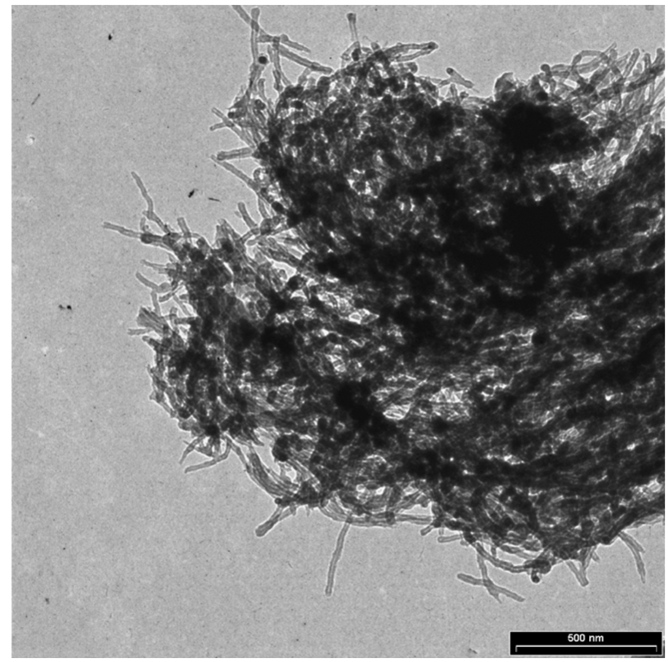

Fig. 5. TEM image showing agglomeration of carbon nanotube in MgB_2 with nanotube diameter 8–15 nm.

rapidly with the increasing of distortion. T_c drops to 34.4 K with the shift of a by -0.1252 Å for 20–30 nm CNT doped MgB_2. For the sample of 60–100 nm CNT doped MgB_2 its T_c was 37 K with 0.0044 Å of a distortion. As suggested by Wilke *et al.*, T_c may be used as an indicator of how much carbon is in the MgB_2 [9].

Fig. 3 shows the TEM image for MgB_2 with CNT of 8–15 nm and 20–30 nm. The image shows that some CNT's are well embedded in the grains of MgB_2 for all diameters of CNT (bright tubes in Fig. 3). EDX results showed that the dark areas are carbon, magnesium and boron phase. The encapsulation of CNT into the superconducting matrix was obtained for the reacting temperature above 600°C. This suggests that the nanotubes could get embedded within the grains before the sintering temperature of 900°C is reached. At the same time this encapsulation restricted the reaction of oxygen with CNT. This unique microstructure provides the samples with a good grain connection for the MgB_2 phase and high density of flux-pinning centers created by the CNT.

However, longer CNT's tend to entangle and agglomerate, that makes mixing inhomogeneous. CNT's with outside diameter <8 nm and 8–15 nm have the longest length of all other nanotubes used. The J_c for the sample was the lowest, as shown in Fig. 4. It should be noted that the inhomogeneous mixing results in a lower value of J_c than for the pure MgB_2. TEM image in Fig. 5 showed that the agglomerated CNT's were found in the CNT doped MgB_2. This suggests that the pinning behavior of the CNT doped MgB_2 strongly depends on the density of the CNT in the samples. We believe that the agglomerated CNT's will block the transport of the current density and suppresses the J_c. This implies that most of the CNT doped MgB_2 samples are not homogenous and may not have even distribution of nanotubes. The same problem was encountered by Galvan *et al.* [10] when they embedded nanotubes in the Bi-based superconductor. This suggests that shorter length nanotubes would be the solution for more homogenous mixing and substitution. TEM studies again confirmed that nanotube-like structures were presented after full processing even at high temperature.

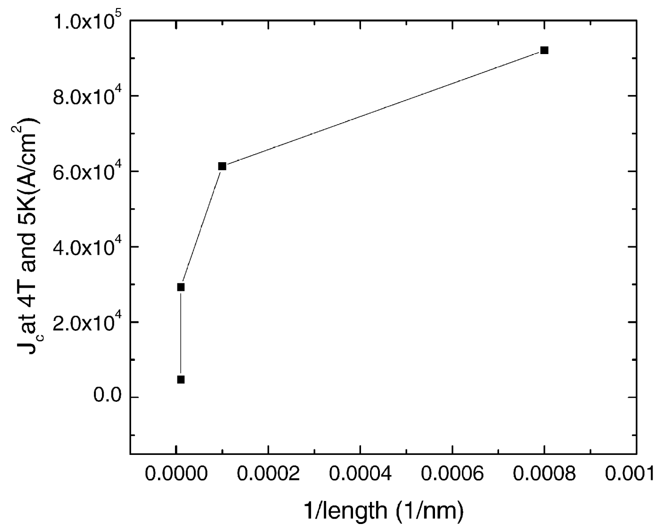

Fig. 6. Dependence of J_c as a function of the average length of nanotubes incorporated into the MgB_2 matrix. The solid line through the points is guide to the eye.

Fig. 6 shows that J_c changed with the length of the CNT. The graph indicates that shorter length of CNT will result in a better incorporation of CNT into the MgB_2 matrix, because longer CNT tend to agglomerate by entangling with each other. As a result, the main factor to defining the degree of incorporation of CNT in MgB_2 will be the length of nanotubes instead of their diameter. This is also the reason for not obtaining the correlation between the diameter of CNT and the lattice parameter a, and therefore T_c. An improved preparation method has been carried out and the results will be published elsewhere.

IV. Conclusion

Carbon nanotubes with different geometry were used as dopant to MgB_2. The CNT doping significantly enhanced $J_c(H)$ performance in magnetic field. Nanotubes are seen to adhere to the MgB_2 matrix for all the samples, with some proportion of them appearing as agglomerates which caused inhomogeneity in CNT doped MgB_2. This agglomeration was worsened with increasing length of CNT. This suggests that extra care should be taken to the sample preparation method if dealing with nanotube doping particles.

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