Alignment of Carbon Nanotube Additives for Improved Performance of Magnesium Diboride Superconductors**

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The rapid progress in developing MgB2 superconductors since its relatively recent discovery[1] has made this material a strong competitor to other low- and high-temperature superconductor (HTS) materials for technological applications, especially in niche markets such as magnetic resonance imaging (MRI). Thanks to the lack of weak links and the two-gap superconductivity of MgB2,[2,3] a number of different additives have been successfully used to enhance the critical current density, $J_c$, and the upper critical field, $H_{c2}$.[4–12] Carbon nanotubes (CNTs) have unusual electrical, mechanical, and thermal properties,[13–16] and hence are ideal components for inclusion in composites to improve composite performance. To take advantage of the extraordinary properties of CNTs, it is important to align the CNTs in the composites. Here, we report a method for aligning CNTs in CNT–MgB2 superconductor composite wires through a readily scalable drawing technique. The aligned-CNT-doped MgB2 wires show an enhancement in magnetic critical current density, $J_c(H)$, by more than one order of magnitude under high magnetic fields compared to the undoped samples. The CNTs also significantly improve heat transfer and dissipation. CNTs have mainly been used in structural materials, but here the advantages of their use in functional composites are demonstrated, which has wider ramifications for other functional materials.

High in-field $J_c$ of MgB2 superconductors is a major requirement for large-scale applications. In addition, MgB2 wires need to exhibit good mechanical properties and thermal stability. The additives studied so far have mainly been used to improve $J_c(H)$ by introducing effective pinning sites in MgB2. Not much attention has been focused on the mechanical and thermal properties of the MgB2 wire core. Among the additives that have been studied, CNTs have the potential to additionally improve the mechanical and thermal properties of the MgB2 wires, since they have been used as reinforcing components in a number of different composites.[17,18] Fosheim et al. have reported an enhanced flux pinning in Bi2Sr2CaCu2OB2+x superconductors with embedded CNTs.[19] Yang et al. have discovered a significant enhancement in $J_c(H)$ for HTSs by introducing nanorods as columnar pinning centers in the composites.[20–22] We previously reported that CNT doping enhanced $J_c$ under magnetic fields for bulk MgB2.[12,23] However, in that case the CNTs were randomly dispersed in bulk MgB2. Inspired by the previous reports, in this communication we report a technique for aligning CNTs in Fe-sheathed MgB2 wires. The advantages of doping with CNTs rather than other additives are: 1) Multiwalled CNTs can carry current densities up to $10^9$–$10^{10}$ A cm$^{-2}$ (compared to a typical value of $10^5$–$10^6$ A cm$^{-2}$ for superconductors), and remain stable for extended periods of time;[14] CNT doping can thus improve the current path and connectivity between the grains in MgB2. 2) The thermal conductivity for isolated multiwalled CNTs is estimated to be about 3000 W mK$^{-1}$,[15] and hence could enhance heat dissipation and thermal stability of the MgB2 wires. 3) Bundled CNTs have a very high axial strength and stiffness, approaching values for an ideal carbon fiber.[16] If CNTs could be aligned along the longitudinal axis of the MgB2 wires, it is expected that they would significantly improve the mechanical properties of the CNT–MgB2 composite wire. 4) Finally, CNTs are one-dimensional (1D) materials with very large aspect ratios and can act as line-pinning sites instead of the point-defect-pinning sites provided by other additives. We demonstrate that a high degree of CNT alignment can be readily achieved by mechanical drawing in the powder-in-tube (PIT) process. The aligned CNT-doped MgB2 wires show a significant enhancement in flux pinning and heat transfer.

Figure 1 shows $J_c(H)$ calculated from magnetization hysteresis loops with the magnetic field, $H$, applied both parallel
and perpendicular to the wire axis, \( a \), for both undoped and CNT-doped MgB\(_2\) wires. It is noted that for the undoped MgB\(_2\) wire, there is a small difference in \( J_c(H) \) along the two measured field directions due to the wire-drawing process. In contrast, for CNT-doped MgB\(_2\), \( J_c(H) \) shows two characteristic features: a strong anisotropy with regards to the field direction, and a clear enhancement of flux pinning in the high-field region, as compared to the undoped sample. The anisotropy in magnetic \( J_c \) is stronger at 5 K than at 20 K, and the extent of this anisotropy increases with the magnetic field \( H \), ranging from a factor of 2–3 under low fields to more than one order of magnitude under high fields. The enhancement in \( J_c(H) \) performance due to CNT doping is more significant at low temperatures and under higher fields. For example, the magnetic \( J_c \) in the \( H \perp a \) direction increases by a factor of 4 at 20 K and 4 T, and by a factor of 37 at 5 K and 7 T, as a result of CNT doping. What is more striking is that the enhancement in \( J_c \) for the CNT-doped MgB\(_2\) wires occurs with the applied field \( H \) both parallel and perpendicular to the wire axis. \( J_c(H \perp a) \), perpendicular to the wire axis, shows more significant enhancement than \( J_c(H \parallel a) \), parallel to the wire axis, compared to the undoped MgB\(_2\) wire.

X-ray diffraction (XRD) and electron diffraction patterns do not show any evidence for a preferred crystalline orientation of MgB\(_2\) grains in the wire core in either longitudinal or transverse directions relative to the wire axis. This is not surprising since the MgB\(_2\) crystal is formed by an in-situ process in which there is no driving force for MgB\(_2\) crystalline alignment. Thus, the anisotropy measured above is not due to MgB\(_2\) crystallite alignment. Figure 2a shows a scanning electron microscopy (SEM) image of the CNT-doped MgB\(_2\) wire. A strongly elongated macrostructure is clearly evident along the wire axis. In the CNT-doped bulk material, the CNTs are randomly dispersed in the MgB\(_2\) matrix, and most of the CNTs are highly entangled, as shown in Figure 2b. In contrast, for the PIT process, the mixture of Mg and B powder and the CNT additives flow along the wire axis as a result of continuing drawing and reduction processes. The drawing process is repeated more than thirty times to reduce the iron sheath/ Mg + B powder composite from 10 mm in diameter to 1–1.4 mm in diameter. Because of the high aspect ratio of CNTs, the drawing force leads the entangled CNTs to straighten in the longitudinal direction. The degree of CNT alignment increases with an increased number of drawings. For a single-filament MgB\(_2\) wire, the filament diameter is relatively large compared to the CNTs. However, practical conductors are made of multiple filaments with the diameter of each filament being as small as 10 \( \mu \)m, which is comparable to the diameter of the CNTs (up to 2 \( \mu \)m). Thus, a high degree of CNT alignment can be achieved. Nevertheless, the extent of CNT alignment is clearly evident from both magnetic \( J_c \) measurements and transmission electron microscopy (TEM) observations of single-core filaments. Figure 2c shows a TEM image of embedded, straightened CNTs aligned in the same direction in the MgB\(_2\) wire core. The inset shows a high-resolution image of the lattice of one of the CNTs. Figure 2d also shows a TEM image for several parallel CNTs embedded in the MgB\(_2\) matrix. The inset in Figure 2d shows the high-resolution lattice image of one of the CNTs. These results indicate that the anisotropy in \( J_c \) originates from the alignment of CNTs during
the mechanical drawing process. The CNT-induced anisotropy in \( J_c \) is attributable to two factors: high axial conductivity\(^{[14,24]} \) and the large aspect ratio of the CNTs. The CNTs aligned along the core axis are expected to improve the connectivity between grains by bridging poorly connected regions, which helps to overcome an ubiquitous problem for the in-situ reaction process, since the density of MgB\(_2\) only reaches about 50% of the theoretical density for wires fabricated by this process. The better in-field \( J_c \) performance in the longitudinal direction, when the field is applied perpendicular to the wire axis, suggests that the presence of CNTs in the longitudinal direction induces strong pinning sites transverse to the longitudinal axis. This comes as a surprise as we expect exactly the opposite behavior, that is, stronger pinning should occur along the longitudinal direction of the CNTs when the field is applied parallel to the wire axis, since the flux lines are expected to have a strong interaction with the CNTs. However, we must consider that when the CNTs are aligned along the wire axis, the total cross-sectional area of the CNTs transverse to the wire axis is much smaller than in the longitudinal direction due to the high aspect ratio of the CNTs. Thus, the overall interaction between the CNTs and the flux lines is stronger when the field is applied perpendicular to the longitudinal wire axis rather than parallel to the wire axis, and hence the \( J_c \) in the longitudinal direction shows better in-field performance than in the transverse direction. As reported previously, the enhancement in \( J_c \) by CNTs can be attributed to two factors: carbon substitution for B and the role of CNTs as strong pinning centers.\(^{[12,23]} \)

Furthermore, the CNTs have a strong effect on heat transfer during materials processing due to their high thermal conductivity. Figure 3a shows the effect of the heating rate on \( J_c(H) \) behavior for the pure and CNT-doped MgB\(_2\) wires. We note that the heating rate has no effect on \( J_c(H) \) for the CNT-doped MgB\(_2\) wire, while \( J_c(H) \) for the pure MgB\(_2\) wire processed at a rapid heating rate of 15 °C min\(^{-1}\) is lower than that at a slow heating rate of 1.7 °C min\(^{-1}\) by a factor of three. In the rapid heating case, for the pure MgB\(_2\) wire, the solid-state reaction is inhomogeneous due to the large temperature gradient. On the other hand, the CNTs, because of their efficient heat-transfer properties and by acting as nucleation centers, mediate a homogeneous reaction throughout the core. For the slow heating case, there is sufficient time for heat transfer to the interior, and hence the reaction can take place homogeneously in the entire core region. This interpretation is further verified by the differential thermal analysis (DTA) plots for the Fe-sheathed pure MgB\(_2\) and 10% CNT-doped MgB\(_2\) wires with a heating rate of 15 °C min\(^{-1}\), as shown in Figure 3b. There are two exothermic peaks for the pure MgB\(_2\) wires, while for the CNT-doped MgB\(_2\) wires, these two peaks are merged into one broad peak. The first peak is due to the reaction between Mg and B\(_2\)O\(_3\), while the second peak is attributable to the formation of MgB\(_2\).

CNTs, because of their high aspect ratio, are desirable nucleation centers for triggering and propagating MgB\(_2\) formation along their entire length. Since the CNTs have a high thermal conductivity, heat is transferred along the CNTs to the adjacent regions. Thus, the MgB\(_2\) formation reaction takes place with the CNTs as the nucleation centers and propagates along the length of the CNTs. The high thermal conductivity and desirable elongated geometry of the CNTs is responsible for the insensitivity of CNT-doped MgB\(_2\) wires to the heating rate, which is convenient and advantageous for the manufacture of practical conductors.

In summary, the alignment of CNTs in CNT–MgB\(_2\) composite wires has been achieved by a readily scalable drawing technique. The aligned CNT-doped MgB\(_2\) wires show an enhancement of the magnetic \( J_c \) by more than an order of magnitude under high-field conditions. The aligned CNTs induce anisotropy in magnetic \( J_c \) with respect to the direction of the applied field and significantly improve heat transfer and dissipation during materials processing. In addition to the benefits of the electrical and thermal conductivity of CNT doping, the alignment of CNTs along the wire axis is expected to lead to enhancements of mechanical properties such as tensile strength and flexibility due to the unique axial strength of CNTs. Studies on these properties are underway.

**Experimental**

CNT-doped MgB\(_2\) wires were prepared using the PIT method through an in-situ reaction process. Powders of magnesium (99 %) and amorphous boron (99 %) were well mixed with 0 and 10 wt.-% randomly distributed multwall carbon nanotubes (outer diameter (OD): 20–30 nm, length: 0.5–2 μm) and thoroughly ground. An ultrasonic mixer was used to improve the homogeneity of the mixed Mg, B, and CNTs.
The Fe tube had an OD of 10 mm and a wall thickness of 1 mm, and was 10 cm long with one end of the tube sealed. The mixed powder was filled into the tube and the remaining end was blocked using an aluminum bar. The composite was drawn to a 1–1.4 mm diameter wire through a series of more than 30 dies with a reduction rate of about 10% in every drawing. For fabrication of multifilament wires, a bundle of single-core wires was inserted into an iron tube, and the composite was drawn into a 1–1.4 mm diameter wire. Several short samples, 2 cm in length, were cut from the wire. These pieces were then sintered in a tube furnace at 800 and 830°C for 30 min at a heating rate of 3°C min⁻¹, and finally furnace-cooled to room temperature. A high-purity argon gas flow was maintained throughout the sintering process. An undoped sample was also made under the same conditions for use as a reference sample. Sintering of wires at different heating rates was carried out at Cambridge. Two heating rates of 1.7 and 15°C min⁻¹ were used, followed by isothermal annealing at 850°C for 30 min. The samples were then furnace-cooled to room temperature. The phase and crystal structures of all the samples was obtained from XRD patterns measured using a Philips (PW1730) diffractometer with CuKα radiation. DTA was performed to study the effect of the heating rate on Jc. The grain morphology and microstructure were also examined by a SEM equipped with a focused ion beam (FIB) apparatus and by TEM. The magnetization was measured up to 8.5 T. Bar-shaped samples with a diameter of 0.7 mm and length of 2.7 mm were cut from the wire core for magnetic measurements. The magnetic field was measured up to 8.5 T.

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