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**Improvement of Upper Critical Field and Critical Current Density in Single Walled CNT Doped MgB2-Fe Wires**

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Improvement of Upper Critical Field and Critical Current Density in Single Walled CNT Doped MgB₂/Fe Wires


Abstract—We evaluated the doping effect of single walled carbon nanotubes (SWCNT) on the phase formation, microstructure, critical current density ($J_c$), and upper critical field ($H_{c2}$) of MgB₂ superconductor. All samples were sintered at temperatures ranging from 650 to 1000°C for 30 min. A typical high sintering temperature (900°C) sample was composed of well-consolidated MgB₂ grain of 100 to 200 nm and nanosized particles, resulting in enhancement of $J_c$ and $H_{c2}$. This indicates that lattice defects and microstructural change have occurred as a result of carbon (C) coming from SWCNT. On the other hand, a sample sintered at low temperature (700°C) contained relatively large grains. Specifically, SWCNT doped MgB₂ wire sintered at 900°C exhibited excellent $J_c > 10^4$ A.cm⁻² up to 8 T at 4.2 K. This result indicates that flux pinning for sample produced at a high sintering temperature are enhanced by SWCNT doping. SWCNT is one of the promising C sources for MgB₂ superconductor with excellent $J_c$.

Index Terms—Critical current density, MgB₂, single walled carbon nanotube, upper critical field.

I. INTRODUCTION

With a high critical temperature ($T_c$) of 39 K, MgB₂ superconductor is one of the most promising materials for applications [1]. However, the current density ($J_c$) of un-doped MgB₂ is sharply depressed due to poor flux pinning as the magnetic field is increased. From the applications point of view, the effect of carbon (C) doping on the upper critical field ($H_{c2}$) and $J_c$ of the MgB₂ is critical. Recently, many groups have studied C containing compounds and composites, such as SiC, B₄C, and carbon nanotubes (CNTs), finding that they improved the $H_{c2}$($H_{irr}$) and $J_c$ of MgB₂ [2]–[6]. A record high $H_{irr}$ of 29 T and $H_{c2}$ of 37 T have been achieved for nano-SiC doped wire at 4.2 K. However, SiC doped MgB₂ has a poor thermal and electrical properties. On the other hand, CNTs have excellent thermal, electrical, and mechanical properties [7]. For example, CNTs can carry current densities up to $10^9$ to $10^{10}$ A.cm⁻² and remain stable for extended periods of time. The CNT addition may improve the connectivity between grains. The thermal conductivity for CNTs is about 3000 W.m⁻¹.K⁻¹ and could benefit the heat dissipation and thermal stability of the MgB₂ wires. In addition, CNTs have axial strength and stiffness, approaching that for ideal C fiber. If aligned, CNTs could improve the mechanical properties of MgB₂-CNT composite wire. What is worth noting is that CNT can be used as a C source. In the literature, differences in the reactivity of CNT are attributed to the number or size of CNT open end [8]. In general, as the single walled CNT (SWCNT) have a much smaller diameter compared to multi walled CNTs (MWCNTs), a much larger number of open ends can be introduced in SWCNTs. In our study, therefore, we evaluated the doping effect of SWCNT on MgB₂ superconductor.

II. EXPERIMENTAL PROCEDURE

A. Single Walled CNT

Table I illustrates the main specifications of SWCNT. Co-Mo/SiO₂ along with pre-existing SWCNTs was used as a catalyst for the generation of CNTs. Fig. 1 shows a high resolution transmission electron microscope (HRTEM) image...
of the SWCNTs created. The SWCNTs were assembled into bundles. The diameter of each SWCNT ranged from 0.9 to 1.8 nm. Small quantities of amorphous C were observed covering the bundles of SWCNTs.

B. Sample Preparation and Evaluation

SWCNT doped MgB$_2$ composite wire was fabricated by an in-situ powder-in-tube (PIT) process. The detailed procedures for making wires have been reported elsewhere [5]. Magnesium (Mg, 99%), Boron (B, 99%), and SWCNT powders were used as starting materials with the composition of MgB$_{2-x}$C$_x$O$_{2.2}$ because this composition resulted in the highest $T_c$ in our group of samples. The mixed powders were packed into iron (Fe) tubes with $L = 140$ mm. The Fe tube had an outer diameter (O.D.) of 10 mm and an inner diameter (I.D.) of 8 mm. The composites were drawn to an O.D. of 1.42 mm. The fabricated wire was sintered at 650 to 1000°C for 30 min under high purity Ar gas, and then cooled in the furnace. Un-doped MgB$_2$ wire was also fabricated for comparison by applying the same processing. The heating rate was 5°C min$^{-1}$. All samples were characterized by x-ray diffraction (XRD), ac susceptibility, transport critical current ($I_c$), and transmission electron microscopy (TEM).

III. RESULT AND DISCUSSIONS

Fig. 2 shows the XRD patterns of SWCNT doped MgB$_2$ sintered at different temperatures. All samples seemed to be well-developed MgB$_2$ with a small amount of MgO. All XRD patterns were independent of the sintering temperature. At 1000°C, however, there was Fe$_2$B in the layer between the Fe sheath and the superconductor core. This is attributed to the phase transformation of Fe at 910°C. It is to be noted that the relative intensity of MgO does not change with sintering temperature. The calculated values, MgO(220)/MgB$_2$(102) were 1.05, 0.99, 1.00, 1.00, and 0.99 for the corresponding sintering temperatures. In the case of MgO formation, there are two possibilities: (1) the Mg surface of the starting powder has already oxidized in air because Mg could act as an oxygen getters (2) Mg can react with O to form MgO at around 450°C during the sintering process.

Fig. 3 shows the $T_c$ of samples sintered at different sintering temperature from 650 to 1000°C. As the sintering temperature increased to 700°C, the $T_c$ value increased a little. This is related to the improved crystallinity of MgB$_2$ samples when there is higher temperature sintering, but no C substitution. As the sintering temperature further increased to 1000°C, however, the $T_c$ of samples decreased monotonically. This is attributed to C substitution in B sites. In our previous work, $T_c$ was depressed in proportion to the amount of C substituted in a given sample [9]–[11]. Even though the nominal composition remains the same, a higher sintering temperature results in more C substitution for B.

From XRD, we also calculated the $a$- and $c$-lattice parameters. For example, the sample sintered at 900°C had $a$- and $c$-lattice parameters of 3.0712 Å and 3.5242 Å, respectively. It is to be noted that the $c$-axis parameter did not change with sintering temperature. What is worth noting is that more C is substituted in B sites in SWCNT doped MgB$_2$ than in nano-C doped samples [3]. This result indicates that C coming from SWCNT is more active compared to nano-C.

Fig. 4 shows TEM images of samples sintered at (a) 700°C and (b) 900°C. In all samples, the powder was suspended on “lacy carbon grids,” that is, a network of carbon filaments. In Fig. 4 (a), an agglomerate of un-reacted CNTs can be seen at the edge of the MgB$_2$ (arrowed). Two features which appear to be CNTs mixed into MgB$_2$ are indicated by arrows. A number of fine particles, 5 to 10 nm in size, are present. It is not clear whether they are CNTs which have been ground up and made smaller by the consolidation process. In addition, the MgB$_2$ was seen to be fine grained, with a 100 to 200 nm grain size, but containing some pores so that well consolidated. On the other hand, dislocation can be seen and a few un-reacted CNTs (marked by arrows) are also visible in Fig. 4(b). From energy dispersive x-ray (EDX) spectra, nanosize particles in the matrix were rich in oxygen, which was consistent with MgO. These could act as strong flux pinning centers.

Fig. 5 shows the transport $J_c$ of SWCNT doped MgB$_2$ wires sintered in the high sintering temperature range of 800 to 950°C. Sample sintered at high temperatures also had good $J_c$ in our previous work [5], [9]. This is attributed to greater C substitution coming from CNTs. The $J_c(B)$ of un-doped MgB$_2$ wires sintered at 650°C and 900°C is also plotted for comparison and reference. It was observed that $J_c$ for SWCNT doped MgB$_2$ was higher than that for un-doped MgB$_2$. Specifically, the SWCNT
The wire with wire were higher than those of un-doped wires sintered at superconductor sintered at (a), and exhibited excellent wires sintered at 650°C. This indicates that for 30 min. It was observed that a typical high sin-
were 3.0712 wire sintered at (a) wire with the best (a) was composed of well-con-
of un-doped wire. This is be-
values in the range form 8 T to 12 T were a little decreased. This is related to greater C substitution in B sites. This observation is further supported by the $T_c$ results on the SWCNT doped MgB$_2$, as mentioned above.

Fig. 6 shows the $H_{c2}$ of the SWCNT doped MgB$_2$ wire with the best $J_c(B)$. The $H_{c2}$ of un-doped MgB$_2$ wires sintered at 650°C and 900°C is also plotted for comparison and reference. As can be seen in figure, the $H_{c2}$ and $dH_{c2}/dT$ of SWCNT doped MgB$_2$ wire were higher than those of un-doped MgB$_2$ wire below 25 K. The un-doped MgB$_2$ wire sintered at 650°C also had a better $H_{c2}$ than the 900°C un-doped wire. This is because a small MgB$_2$ grain size allows the extra grain boundaries to also act as strong flux pinning centers.

IV. CONCLUSIONS

We evaluated the doping effect of SWCNT on the phase formation, microstructure, $J_c$, and $H_{c2}$ of MgB$_2$ superconductor. All samples were sintered at temperatures ranging from 650°C to 1000°C for 30 min. It was observed that a typical high sintering temperature sample (900°C) was composed of well-consolidated MgB$_2$ grains of 100 to 200 nm and nanosized particles, resulting in enhancement of $J_c$ and $H_{c2}$. This indicates that lattice distortion and microstructural changes have occurred as a result of C coming from SWCNT. From XRD, the $c$-and $c$-lattice parameters of the SWCNT doped MgB$_2$ sample sintered at 900°C were 3.0712 Å and 3.5242 Å, respectively. On the other hand, a sample sintered at low temperature (700°C) contained relatively large grains. Specifically, SWCNT doped MgB$_2$ wire sintered at 900°C exhibited excellent $J_c$ ~ $4 \times 10^3$ A/cm$^2$ at 12 T at 4.2 K. This result indicates that flux pinning for sample produced at a high sintering temperature is enhanced by more C substitution coming from SWCNT. In addition, the $H_{c2}$ and $dH_{c2}/dT$ of SWCNT doped MgB$_2$ wire were higher than those of un-doped MgB$_2$ wire below 25 K.
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