Fabrication and Characterization of the MgB$_2$ Bulk Superconductors Doped by Carbon Nanotubes

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Abstract—Carbon nanotube (CNT) doped MgB$_2$ with $0.1\%$ at CNT bulk superconductors were fabricated using an in-situ technique to improve the critical current density ($J_c$) in a high magnetic field. The effects of doping and the sintering temperature on the phase formation, microstructure, and critical properties were evaluated. Two types of the CNT were used as dopants: the conventional CNT ($C_{\text{CNT}}$) with a mixture of large and small diameter (5 and 20 nm) and the small CNT ($S_{\text{CNT}}$) with 5 nm diameters.

For both CNT-doped samples, the a-axis lattice parameter decreased but its reduction was more significant at 900°C than at 800°C. The decrease in $T_c$ was consistent with the change in the a-axis lattice parameter, which is probably due to the effect of C substitution for the B sites in MgB$_2$. The $J_c$ of the doped samples decreased more slowly with increasing magnetic field than that of the undoped samples. In addition, the $S_{\text{CNT}}$-doped sample exhibited superior $J_c$ ($B$) behavior than the $C_{\text{CNT}}$-doped sample. This was partly attributed to the higher doping level and the presence of finer CNTs, which acts as an effective pinning center.

Index Terms—Carbon nanotube, critical current density, doping, in-situ, MgB$_2$.

I. INTRODUCTION

The discovery of superconductivity in the intermetallic compound, MgB$_2$, has attracted considerable interest on account to its high transition temperature ($T_c$) of 39 K. Recently, many groups have demonstrated the intrinsic properties of the grain connectivity, large coherence lengths, and low anisotropy, which make it a potential material for practical applications. However, MgB$_2$ has a low upper critical field ($H_{c2}$) and exhibits a relatively rapid decrease in critical current density ($J_c$) under high magnetic field, which needs to be improved before it can be used in high field applications.

Chemical doping is a prospective technique for improving the $J_c$ performance at high magnetic field, and a number of different doping elements have been examined. The substitution of C for the B sites leads to intraband scattering that increases the $H_{c2}$, as reported by many groups. Among the various C sources, such as SiC [1], graphite [2], B$_4$C [3], and carbon nanotubes (CNT) [4]–[7], CNT have attracted particularly interest on account of their geometry, which may make them a more effective type of flux pinning center. The effects of CNT doping on the critical properties have been reported by several groups and both $J_c$ and $H_{c2}$ were improved by CNT doping into MgB$_2$ [4]–[7]. Specifically, Dou et al. [6], studied the effect of sintering temperature on properties of CNT-doped MgB$_2$ [4] and Yeoh et al. [6] and Serano et al. [7] evaluated the geometric effects of CNTs as C source in MgB$_{2-x}$C$_x$. It is believed that the critical properties can be improved further when roles of the CNT geometry and its components such as metallic or semiconducting CNT are understood and the sintering temperature is optimized systematically.

In this study, two types of CNTs were used as the C source: conventional CNTs and CNT smaller than conventional CNT [8]. Using the two types of CNTs, a nominal composition MgB$_{1.9}$ with $0.1\%$ at CNT bulk sample was fabricated, and the effects of CNT doping and sintering temperature on the phase formation, microstructure, and $T_c$ and $J_c$ were evaluated.

II. EXPERIMENTAL DETAILS

The C-doped MgB$_2$ (MgB$_{1.9}$) bulk superconductor was fabricated by a powder metallurgy technique using an in-situ reaction method. Two types of CNTs were used as the doping element: one is conventional CNTs consisting of larger-and smaller-diameter CNTs and the other has smaller-diameter CNT which was separated from the conventional CNT using the removing technique as described in our previous study [8]. The larger and smaller diameter CNTs are known to be metallic and semiconducting CNT, respectively [8], and their respective diameter was approximately above and below 10 nm. Both the conventional and semiconducting CNTs were consisted of single wall CNT as major part and multi wall CNT as minor one.

Magnesium (Tangshan 325 mesh, 99.9%), amorphous Boron (Tangshan, 99.9%), and conventional CNT (Carbon Nanotechnologies Inc.) or smaller CNT were mixed and agitated supersonically for 1 hr in an Ar atmosphere. The mixed powders were pressed into 10 mm diameter and 1.5 mm thick pellets under a uni axial pressure of 500 MPa, followed by sintering at 800°C and 900°C in a flowing Ar atmosphere. An undoped MgB$_2$ bulk sample was also made using the same procedure for comparison. The undoped, conventional CNT-doped, and smaller CNT-doped MgB$_2$ samples sintered at 800°C and 900°C are hereafter denoted as the undoped-800, $C_{\text{CNT}}$-800, and $S_{\text{CNT}}$-800.
800 and undoped-900, $C_{\text{CNT}} = 900$, and $S_{\text{CNT}} = 900$, respectively.

The crystalline structure and phase formation were examined by powder X-ray diffraction (XRD) using a Bruker D8 Discover diffractometer with CuK$_\alpha$ radiation. The change in the lattice parameters was calculated using the EVA program based on Rietveld refinement analysis from the (002) and (100) peaks. The microstructure was also observed by transmission electron microscopy (TEM, JEOL, JEM 3010). The magnetic $J_c$ and $T_c$ values were calculated from the measured magnetization using a magnetic property measurement system (MPMS, Quantum design) as a function of temperature and applied magnetic field, which was derived from the height of the magnetization loop using Bean’s model [9].

III. RESULTS AND DISCUSSION

Fig. 1(a) shows the XRD patterns of the undoped and doped samples sintered at 800$^\circ$C and 900$^\circ$C. The undoped-800 and 900 samples showed the XRD peaks for MgB$_2$ as the major phase and MgB$_4$ with MgO as the secondary phase. However, there was a higher concentration of the MgB$_4$ phase in the undoped-900 sample than in the undoped-800 sample. It is believed that Mg evaporates more easily at higher temperatures, causing an increase in the amount of Mg deficient phase, MgB$_4$, at 900$^\circ$C. From the XRD pattern of the C$_{\text{CNT}} = 800$ and 900 samples, a CNT related peak was observed at approximately 26.6$^\circ$ while this peak was undetectable for the S$_{\text{CNT}}$-doped sample due to its diameter being too small (5 nm) to be detected by XRD [10].

The change in the a- and c-axis in the MgB$_2$ samples doped with CNT was measured from the (002) and (100) peaks, as shown in Fig. 1(b). For the undoped samples, the $2\theta$ values of the (100) and (002) peak were unchanged. In contrast, for doped samples, $2\theta$ values of the (100) peaks changed but those of the (002) peaks remained relatively unchanged. At 800$^\circ$C, the $2\theta$ values of the (100) peak for the undoped, C$_{\text{CNT}}$-doped, and S$_{\text{CNT}}$-doped sample were 33.59$^\circ$, 33.61$^\circ$, and 33.63$^\circ$, respectively. The corresponding values for the samples sintered at 900$^\circ$C were 33.58$^\circ$, 33.64$^\circ$, and 33.69$^\circ$. It should be noted that the position of the (100) peak of the C$_{\text{CNT}}$-doped samples shifted to a higher angle than that of the C$_{\text{CNT}}$-doped samples with increasing sintering temperature to 900$^\circ$C.

As shown in Fig. 1(b), (100) peaks are sharp and symmetric and have high intensity so that it was easy to define peak position/shift. On the other hand, for (002) peaks, it was difficult to confirm the peak position due to their asymmetric shape and low intensity. Therefore, in order to estimate the change of lattice parameter as C doping, we used Rietveld refinement analysis in which not only a (002) peak but all MgB$_2$ peaks were used in the calculation. As shown in Fig. 2, the a-axis lattice parameter for the undoped, C$_{\text{CNT}}$-doped, and S$_{\text{CNT}}$-doped sample sintered at 800$^\circ$C was 3.0873 Å, 3.0829 Å, and 3.0781 Å, respectively. The corresponding a-axis lattice parameters for the undoped, C$_{\text{CNT}}$-doped, and S$_{\text{CNT}}$-doped samples sintered at 900$^\circ$C were 3.0871 Å, 3.0783 Å, and 3.0721 Å, respectively. On the other hand, for all samples, c-axis lattice parameters remained relatively constant in the range of 3.5240 Å–3.5249 Å. The a-axis lattice parameter decreased for both CNT-doped samples but its reduction became more significant at 900$^\circ$C. The a-axis lattice parameter of C$_{\text{CNT}} = 900$ was similar to that of S$_{\text{CNT}} = 800$, indicating that a similar amount of C had substituted for the B sites in the MgB$_2$ structure. It is believed that S$_{\text{CNT}}$ decomposes and dopes the lattice more easily than C$_{\text{CNT}}$ due to its smaller diameter. Based on the equation relating the a-axis lattice parameter and real C content [11], for the C$_{\text{CNT}}$- and S$_{\text{CNT}}$-doped samples, the real doped C content was calculated to be 0.014 at% and 0.028 at% at 800$^\circ$C, and 0.028 at% and 0.048 at% at 900$^\circ$C, respectively, which is much smaller than the nominal content. In addition, these values were also smaller than those reported elsewhere in that other C sources were used [1]–[3].

Fig. 3 is TEM images showing the remained CNTs for the C$_{\text{CNT}} = 800$ and S$_{\text{CNT}} = 800$ samples. For both samples, both CNTs were located either at the grain boundary or at surface of a porous MgB$_2$ microstructure. In addition, CNTs with two different diameters, 5 nm and 20 nm, were found in the C$_{\text{CNT}} = 800$ sample, which corresponds to the semiconducting and metallic component CNTs, respectively (Fig. 3(a)). On the other hand, the S$_{\text{CNT}} = 800$ sample contained only semiconducting CNTs (Fig. 3(b)). It is believed that S$_{\text{CNT}}$ can act as effective pinning center because its diameter (5 nm) is smaller than the coherency length of MgB$_2$ (6–7 nm), which suggests that the S$_{\text{CNT}}$-doped sample may have improved $J_c$ behavior than the C$_{\text{CNT}}$-doped sample.

Fig. 4 shows the $T_c$ (10% onset) of the undoped and doped samples determined using magnetization method. The $T_c$ of the
undoped-800 and 900 was measured to be 36.9 K and 37.1 K, respectively. The $T_c$ decreased to 36.8 K and 36.6 K for the C$_{CNT}$-doped samples, respectively, and to 36.6 K and 36.3 K for the S$_{CNT}$-doped samples, respectively. This variation showed a similar trend to that of the a-axis lattice parameters: for the C$_{CNT}$-doped samples, the decrease in $T_c$ with increasing sintering temperature was less than that of the S$_{CNT}$-doped samples. Moreover, the $T_c$ value of the S$_{CNT}$ – 800 sample was similar to that of the C$_{CNT}$ – 900 sample, suggesting that the amount of C substitution for B sites in the MgB$_2$ structure is similar for both samples, as noted earlier. The shrinkage of the a-axis lattice parameter and the decrease in $T_c$ are due to differences in the atomic size and number of valence electrons, respectively, as a result of C substitution for B sites [12].

Fig. 5 shows the $J_c$ of undoped, C$_{CNT}$-doped, and S$_{CNT}$-doped samples at 5 K and 20 K in an applied magnetic field up to 5 T. For all samples, the $J_c$ values decreased monotonically with increasing magnetic field, and the degree of the decrease was larger at 20 K. In addition, for the undoped sample, $J_c$ decreased more rapidly than those of the CNT doped samples at both 5 and 20 K, and the degradation was more significant when sintered at 900°C, compared with that observed at 800°C. The slower degradation of the $J_c$ value at 800°C was attributed to its smaller grain size, which provides a stronger grain boundary pinning effect.

At 5 K, the C$_{CNT}$ – 900 sample had the lowest $J_c$ values over the whole range of magnetic fields. On the other hand, the $J_c$ behavior was expected to improve at the higher magnetic field over 5 T because of its slower decrease. The $J_c$ of the S$_{CNT}$ – 900 sample had a crossover at approximately 2.8 T for the undoped-800 sample, and 4.2 T for the S$_{CNT}$ – 800 sample. Similarly, at 20 K, the $J_c$ values of the S$_{CNT}$-doped samples were higher than those of the other samples over the entire range. The $J_c$ of the S$_{CNT}$ – 800 sample was highest at 0.8 T and the S$_{CNT}$ – 900 sample had a crossover at 2.6 T. This $J_c$ behavior is believed to be due to the doping level for S$_{CNT}$ – 900 being higher than that of the other samples, as indicated by the real carbon content from XRD analysis, and the remaining S$_{CNT}$ possibly acting as an effective pinning center.

In order to evaluate the field dependence of the pinning force density ($F_p/F_{p,max}$) at 20 K, the flux pinning force ($F_p$) of the samples was calculated from the hysteresis in the magnetization curves, and then normalized to a maximum value of each sample, as shown in Fig. 6. The $F_p/F_{p,max}$ values of all doped samples were larger than that of the undoped-900 sample above 1.6 T. The $F_p/F_{p,max}$ value of S$_{CNT}$ – 900 was the highest at above 2.0 T. This was attributed to the effect of the band filling of $\sigma$ as a result of C substitution for the B sites as well as the increase in flux pinning centers by the remaining S$_{CNT}$. Overall,
would be more suitable for improving the $J_c$ value of MgB$_2$ in a high magnetic field than C$_{CNT}$.

IV. CONCLUSIONS

The C$_{CNT}$- and S$_{CNT}$-doped MgB$_2$ were fabricated and sintered at 800°C and 900°C. The effects of doping and sintering temperature on the microstructure and critical properties were evaluated. For both CNT-doped samples, the a-axis lattice parameter decreased with decrease being more significant at 900°C than at 800°C. At the same sintering temperatures, the a-axis lattice parameter of the S$_{CNT}$-doped sample decreased more than that of C$_{CNT}$-doped, indicating that S$_{CNT}$ was more effective in substituting for B sites in the MgB$_2$ structure. The decrease in $T_c$ was consistent with the change in a-axis lattice parameter.

The $J_c$ of the doped samples decreased more slowly with increasing magnetic field and had a higher value at a high magnetic field than the undoped samples. In addition, the level of $J_c$ degradation with increasing magnetic field of the S$_{CNT}$-doped sample was smaller than that of the C$_{CNT}$-doped samples. This $J_c(B)$ behavior was attributed to the higher doping level in the S$_{CNT}$-doped sample than in the C$_{CNT}$-doped sample, and that the S$_{CNT}$ can act as an effective pinning center.

REFERENCES