Carbon-coated boron using low-cost naphthalene for substantial enhancement of J_c in MgB$_2$ superconductor

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Abstract

Carbon coating approach is used to prepare carbon-doped MgB$_2$ bulk samples using low-cost naphthalene (C$_{10}$H$_8$) as a carbon source. The coating of carbon (C) on boron (B) powders was achieved by direct pyrolysis of naphthalene at 120 °C and then the C-coated B powders were mixed well with appropriate amount of Mg by solid state reaction method. X-ray diffraction analysis revealed that there is a noticeable shift in (100) and (110) Bragg reflections towards higher angles, while no shift was observed in (002) reflections for MgB$_2$ doped with carbon. As compared to un-doped MgB$_2$, a systematic enhancement in $J_c(H)$ properties with increasing carbon doping level was observed for naphthalene-derived C-doped MgB$_2$ samples. The substantial enhancement in J_c is most likely due to the incorporation of C into MgB$_2$ lattice and the reduction in crystallite size, as evidenced by the increase in the FWHM values for doped samples.

Keywords: MgB$_2$ bulk, naphthalene (C$_{10}$H$_8$), superconducting properties

1. INTRODUCTION

The prime requirement for MgB$_2$ to be useful in practical applications is that it must carry high critical current density (J_c) at high fields and high temperatures [1 $\square$ 3]. The substitution of carbon (C) from C containing compounds into boron (B) sites of MgB$_2$ lattice has been proven to be very effective in pinning the magnetic flux lines (vortices) and maintaining high critical current density at high fields [4 $\square$ 6]. However, the critical current performance is strongly depends on the type of C containing compounds. The oxygen containing C sources, for example, sugar (C$_6$H$_{12}$O$_6$) [7] and other carbohydrates [8] introduce a large amount of oxygen during sintering process, resulting in high content of MgO in MgB$_2$. The insulating MgO is the main obstacle for the transfer of superconducting current between adjacent MgB$_2$ grains and results in a lower critical current density, mainly in the self-field and low-field region [7 $\square$ 8]. Recently, Ye *et al.* used an oxygen free aromatic hydrocarbon, coronene (C$_{24}$H$_{12}$) as an active carbon source [9]. They achieved reasonably good critical current densities in coronene-derived carbon-doped MgB$_2$ wires. However, despite many advantages of coronene, it faces a major drawback of being very expensive. Therefore, in the present study, we used naphthalene (C$_{10}$H$_8$) a low-cost carbon source. Naphthalene has been added into MgB$_2$

before, however, the addition has been done through direct mixing with starting precursor powders of Mg and B [10 $\square$ 12]. Direct mixing may cause poor reactivity of C with B which leads to partial substitution of C into B sites of MgB$_2$, and the remaining C accumulates on the grain boundaries which reduce the connectivity between the grains, and thus the critical current density deteriorates. On the other hand, the process of coating C on B first, then mixing with Mg has proven to be a powerful approach for the effective substitution of C into B, that can improve the performance of MgB$_2$ [13]. Therefore, in the present work, first we coat C on B nano-powders by direct pyrolysis of naphthalene at 120 °C and then the C-coated B powders were mixed well with a stoichiometric amount of Mg. The influence of naphthalene-derived carbon coating on crystal structure and superconducting properties of MgB$_2$ were investigated.

2. EXPERIMENTAL

Naphthalene (C$_{10}$H$_8$), a white powder was used as a carbon source for preparing C-doped MgB$_2$ bulk superconductors. To achieve C-coating on B, the naphthalene of 2.5 to 20 wt. % of total (Mg + 2B) was uniformly mixed with boron nano-powders in a mortar by grinding. Then, the mixed powders were placed into an alumina crucible and heat treated at 120°C (higher than the melting point of naphthalene ~ 80°C) for 30 minutes in Ar atmosphere. The coating of C on B powders was

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anticipated by pyrolysis process. This C-coating process is similar as reported by Ye *et al.* for coronene ($C_{24}H_{12}$) to obtain C-coated B by heat-treating coronene at a temperature above its meting point (438 °C) [9]. After obtaining C-coated B powder, then it was milled properly with an appropriate amount of Mg. The mixed powders were pelletized under 10 ton pressure using uniaxial hydraulic press. Un-doped MgB_2 pellet was also prepared for comparison. The pellets were put into Fe tubes and heat treated at a temperature of 700°C for 30 min under the flow of high-purity Ar gas. Finally, the un-doped and C-doped MgB_2 samples were cooled down to room temperature in a continuous flow of Ar gas.

The crystal structures of un-doped and C-doped MgB_2 samples were investigated by X-ray diffraction (Rigaku, D/Max 2500) using Cu Kα as an X-ray source. The microstructures of samples were examined by field emission scanning electron microscopy (FESEM). The magnetization measurements, magnetization versus temperature (*M-T*) and magnetization hysteresis (*M-H*) loops were carried out on all samples by using a quantum design vibrating sample magnetometer option (PPMS, Quantum Design). The magnetic field varying from -9 T to + 9 T was applied parallel to the longest dimension of the samples. The J_c was estimated from *M–H* loops by Bean's critical state model, $J_c = 20\Delta M/a(1-a/3b)$, where ΔM is the height of the *M–H* loop, *a* and *b* are the thickness and width of the sample, respectively.

3. RESULTS AND DISCUSSION

The phase analysis of un-doped and MgB_2 doped with carbon using different weight percent of naphthalene are performed by X-ray diffraction (XRD) and the patterns are shown in Fig. 1(a). The MgB_2 diffraction peaks are clearly observed along with MgO peaks. From XRD patterns, it is observed that as compared to un-doped MgB_2 the naphthalene-derived carbon-doped MgB_2 samples show a noticeable shift in (100) and (110) Bragg reflections towards higher angles as shown more clearly for (110) in Fig. 1(b), while no shift was observed in (002) reflections. It indicates that the '*a*' lattice parameter was decreased for doped MgB_2, while the '*c*' parameter remains unchanged, which implies that C could be substituted in the B honeycomb layer without affecting the interlayer interactions. In order to estimate the actual level of C substitution for the naphthalene-derived carbon-doped samples of MgB_2 we used the relation, $x = 7.5 \times \Delta(c/a)$, where *x* is the composition of C corresponding to the formula $Mg(B_{1-x}C_x)_2$ and $\Delta(c/a)$ is the change in *c/a* compared to un-doped sample [14]. The C substitution level was observed to be 0.005, 0.005, 0.008 and 0.01 for 2.5, 5, 10 and 20 wt. % of naphthalene-derived carbon-doped MgB_2, respectively. It indicates that with naphthalene of ≤ 5 wt. %, only small C is substituted into MgB_2 lattice, while upon increasing the amount up to 20 wt. % a moderate level of C (*x* =0.01) is substituted. It is noted that the substitution levels of C for the naphthalene-derived C-doped MgB_2 samples are lower than those reported with other sources of carbon [7, 13].
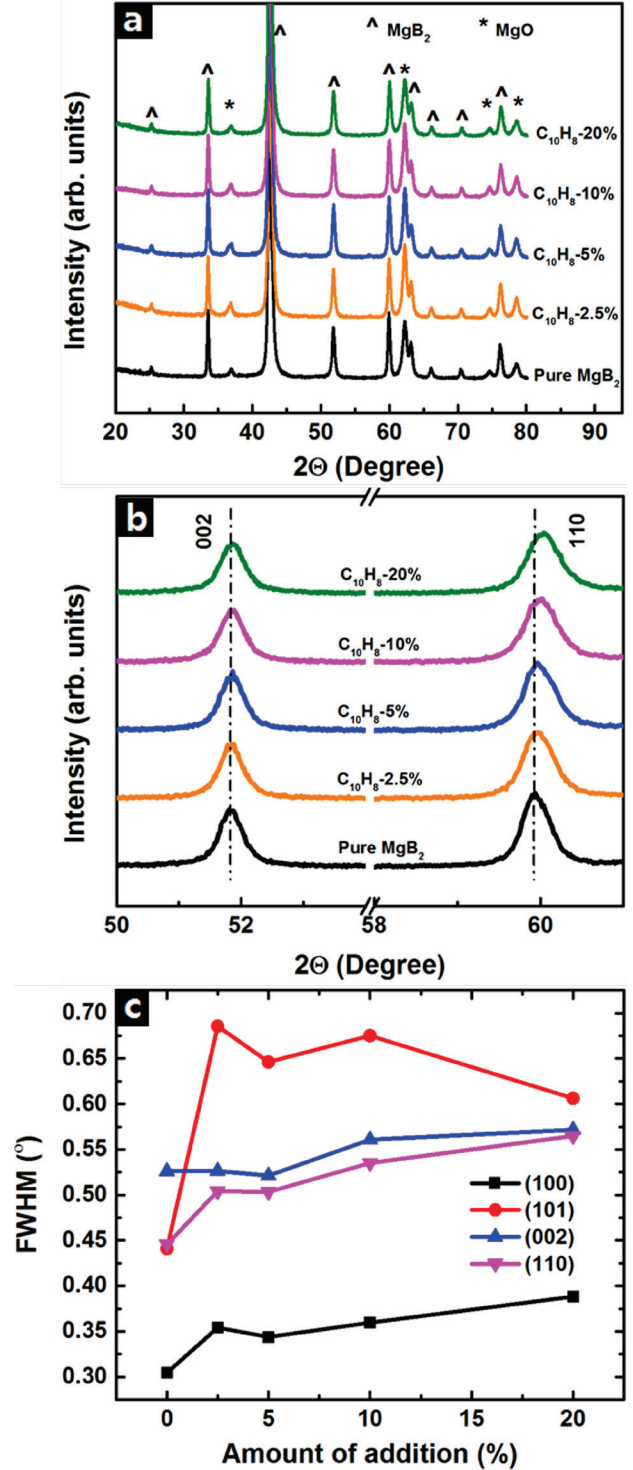

Fig. 1. (a) X-ray diffraction patterns of un-doped and MgB_2 doped with carbon using different weight percent of naphthalene 0 – 20 wt. %. (b) The enlarged view of (002) and (110) Bragg reflections of doped and un-doped samples. (c) The FWHM of (100), (101), (002) and (110) MgB_2 peaks as a function of the amount of naphthalene for all samples.

The low level substitution of C could be attributed to the volatile nature of naphthalene. Since, we have performed the C-coating B process at 120°C, above the melting point of naphthalene (~80°C). At this temperature, the vapor

pressure of naphthalene might be high, so that some of the naphthalene could be easily evaporated without coating onto the B. That could be the one of the reasons of small level substitution of C in doped samples. In our future work, we will try to achieve high doping level of C by performing the C-coating B process close to or slightly above the melting temperature of naphthalene.

Another important feature easily recognized from the XRD figure is the broadening in the diffraction peaks for doped samples. The full width at half maximum (FWHM) values of (100), (101), (002) and (110) MgB$_2$ peaks are plotted as a function of the amount of naphthalene in Fig. 1(c). The FWHM values of all peaks are higher than those of the un-doped sample and they increased with increasing the doping level of naphthalene. The increase in FWHM is a good indication for the reduction in the crystallite size due to carbon doping.

The normalized magnetizations versus temperature curves for the un-doped and the naphthalene-derived carbon-doped MgB$_2$ are shown in Fig. 2. The superconducting transition temperature (T_c) of 37.47 K was obtained for un-doped MgB$_2$. When MgB$_2$ was doped with different weight percent of naphthalene, a decrease in T_c was observed. The T_c of 36.64 K was observed for 2.5 wt. % of naphthalene-derived carbon-doped MgB$_2$ sample, which is suppressed by 0.83 K from that of un-doped MgB$_2$. In overall, a small reduction in T_c of 0.8 to 1.2 K was observed for doped samples. The small drop in T_c is most probably due to the lower level of C was substituted in these doped samples. The suppression of T_c (even though small) for the naphthalene-derived carbon-doped MgB$_2$ samples is more likely due to substitution of C at B sites, as evident by the shrinkage of the 'a' lattice parameter in XRD analysis.

The critical current density as a function of magnetic field for the un-doped and the naphthalene-derived carbon-doped MgB$_2$ samples measured at 5 K and 20 K are shown in Fig. 3. Both at 5 and 20 K, in the high-field region a systematic enhancement in $J_c(H)$ properties with increasing carbon doping level was observed as compared to un-doped MgB$_2$. The substantial enhancement in J_c for doped samples is most likely due to the incorporation of carbon into MgB$_2$ lattice and the reduction in crystallite size, as evidenced by the increase in the FWHM values, both contribute in the pinning of magnetic vortices and result in the improved superconducting performance.

It is interesting to note that at 20 K and in the self-field, the C-doped MgB2 samples show nearly comparable J_c compared to that of un-doped MgB2. This self-field J_c behavior is quite similar as we obtained recently for MgB$_2$ bulk through C-coated B (core/shell) precursor powder [13]. However, this is in obvious contrast to the directly added C-doped MgB2 bulks, where a reduction in self-field J_c was always noticed due to the accumulation of excess C on the MgB$_2$ grain boundaries and thus the reduced connectivity [7, 8]. It indicates that the inter-grain connectivity of our MgB$_2$ samples was not degraded even after doping with carbon from naphthalene. This might be due to C-coated B (core/shell) structure that could lead the active chemical reaction between C and B, and no much
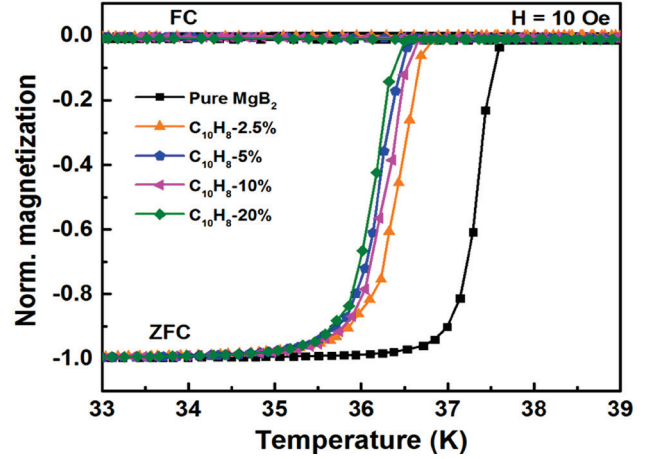

Fig. 2. Temperature dependence of normalized magnetization measured in an applied field of 10 Oe for the un-doped and the naphthalene-derived carbon-doped MgB$_2$. A decrease in T_c was noticed for C-doped MgB$_2$ samples.
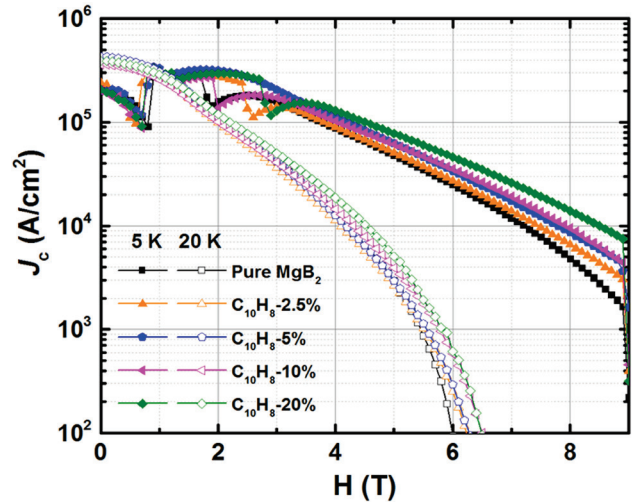

Fig. 3. The critical current density as a function of magnetic field for un-doped and MgB$_2$ doped with carbon using different weight percent of naphthalene measured at 5 K (closed symbols) and 20 K (open symbols). As compared to un-doped MgB$_2$, a systematic increase in J_c with increasing carbon doping level was observed for C-doped MgB$_2$ samples.

extra C could be remained to accumulate on the MgB$_2$ grain boundaries.

4. CONCLUSION

The low-cost naphthalene was used as a carbon source to prepare the carbon-doped and un-doped MgB$_2$ bulk superconductors. As compared to the un-doped MgB$_2$, a reduction in 'a' lattice parameter and suppression of T_c were observed for the naphthalene-derived carbon-doped MgB$_2$ samples. It indicates that the C could be substituted into the B sites of MgB$_2$ lattice. At high magnetic fields, a systematic increase in J_c with increasing carbon doping level was observed for C-doped MgB$_2$ as compared to

un-doped MgB_2. The substantial enhancement in J_c for doped samples is most likely due to the substitution of C into MgB_2 lattice and the reduction in crystallite size, as evidenced by the increase in the FWHM values, both help in the vortex pinning and result in the improved high-field performance.

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