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Influence of oxygen contents of carbohydrate dopants on connectivity and critical current density in MgB$_2$ tapes

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More recently, it has been reported that carbohydrate doping resulted in an effective substitution of carbon for boron in MgB$_2$, and hence achieved significant flux pinning enhancement. However, the authors found that the oxygen amount in carbohydrate additives played an important role in improving J_c-B performance in MgB$_2$. In this work, the effect of maleic anhydride (C$_4$H$_2$O$_3$) and maleic acid (C$_4$H$_4$O$_4$) dopants on the superconducting properties of *in situ* MgB$_2$ tapes has been studied. Compared to the undoped counterpart, both doped tapes showed an enhancement of J_c values by more than an order of magnitude in high-field region; however, the transport J_c of C$_4$H$_4$O$_4$ doped tapes was apparently lower than that of C$_4$H$_2$O$_3$ added samples. The poor grain connectivity as a result of more MgO and voids formed during the reaction in C$_4$H$_4$O$_4$ doped samples can be responsible for the reduced J_c values. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2790381]

Since the discovery of superconductivity in MgB$_2$ at 39 K, intensive studies have been focused on the improvement of critical current density (J_c) and H_{c2}.[1,2] Several groups have reported a significant enhancement in current carrying ability of MgB$_2$ through C doping in various forms, including SiC,[3–5] C,[6,7] B$_4$C,[8] carbon nanotube,[9] and hydrocarbon.[10] In such samples, C can be incorporated into the MgB$_2$ crystal lattice by replacing boron. This substitution results in the enhancement of impurity scattering of the π and σ bands in MgB$_2$. This scattering has been shown to be responsible for the considerable upper critical field increase.

More recently, it has been demonstrated that carbohydrate doping significantly enhances the H_{c2} and H_{irr} in polycrystalline bulks, as well as in tapes.[11–13] Among various carbon-based dopants, carbohydrates are promising candidates as C source materials for C doping into MgB$_2$. Carbohydrates have many advantages such as low cost, easy finding, production of highly reactive C, and avoidance of agglomeration.[11] On the other hand, carbohydrates consist of carbon (C), oxygen (O), and hydrogen (H), so that the O can easily react with Mg to form MgO, which may enhance the vortex pinning, but also strongly degrade the connectivity if present between MgB$_2$ grains, as seen in O-contaminated MgB$_2$.[14]

It is known that the J_c improvement is related, not only to the flux pinning ability, but also to the good grain connectivity. Unfortunately, most work reported by far mainly focus on the flux pinning enhancement, only few authors have investigated the effects of doping or O contamination on the connectivity between grains in MgB$_2$.[14–16] Up to now, the influence of different oxygen contents in carbohydrate dopants on the connectivity and J_c of MgB$_2$ tapes has not yet been reported. As an unavoidable impurity phase, the oxygen contents of dopants might be sensitive to the current transport property of MgB$_2$ tapes. In this work, different amounts of oxygen is introduced into *in situ* powder-in-tube (PIT) processed MgB$_2$ tapes by maleic anhydride (C$_4$H$_2$O$_3$) and maleic acid (C$_4$H$_4$O$_4$) doping. The effect of different doping contents of oxygen on the microstructure, connectivity, flux pinning, J_c, and H_{c2} of MgB$_2$ tapes is studied.

The MgB$_2$ composite tapes with maleic anhydride (C$_4$H$_2$O$_3$, 99%) and maleic acid (C$_4$H$_4$O$_4$, 99%) doping were prepared by the *in situ* PIT method.[13] The added amounts of C$_4$H$_2$O$_3$ and C$_4$H$_4$O$_4$ into the MgB$_2$ samples were 10 wt % of total MgB$_2$. The C$_4$H$_2$O$_3$ or C$_4$H$_4$O$_4$ was dissolved in acetone. The solution was mixed with an appropriate amount of B powder (amorphous, 99.99%) by ultrasonator with the aim of achieving a more uniform distribution. The mixture was dried in a vacuum oven. After drying, the obtained mixture was mixed with an appropriate amount of Mg powder (325 mesh, 99.8%). These mixed powders were packed into Fe tubes. After packing, the tube was rotary swaged and then drawn to wires of 1.75 mm in diameter. The wires were subsequently rolled to tapes. The final size of the tapes was about 3.8 mm in width and about 0.5 mm in thickness. Pure tapes were also fabricated under the same conditions for comparative study. These tapes were heated at 800 or 850 °C for 1 h, and then followed by a furnace cooling to room temperature. The high purity argon gas was allowed to flow into the furnace during the heat-treatment process to reduce the oxidation of the samples.

Figure 1 presents the XRD patterns of pure, C$_4$H$_2$O$_3$ and C$_4$H$_4$O$_4$ doped tapes heat treated at 800 °C. As can be seen, all samples consist of a main phase, MgB$_2$, but some MgO impurity phase is also detected. Maleic acid melts at about 139 °C, at higher temperatures it loses H$_2$O and forms the

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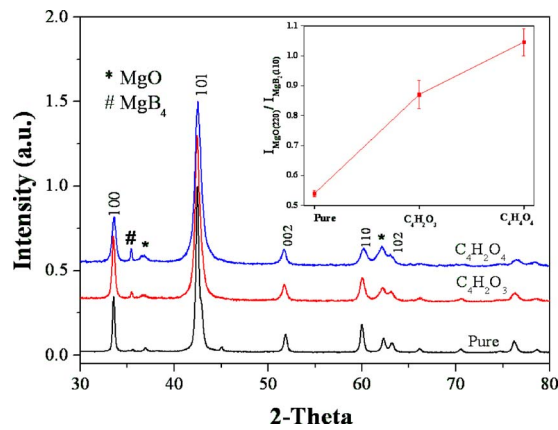
FIG. 1. (Color online) XRD patterns of pure and doped tapes sintered at 800 °C. The peaks of MgB_2 are indexed, while the peaks of MgO and MgB_4 are marked by $*$ and #, respectively. The inset shows the relative intensity of the XRD peak of MgO (220) against the peak of MgB_2 (110).

FIG. 3. (Color online) J_c-B properties of Fe-sheathed pure and doped tapes. The measurements were performed in magnetic fields parallel to the tapes' surface at 4.2 K.

maleic anhydride. Maleic anhydride boils at around 200 °C. The decomposition of the vapor possibly follows the following reaction at 372–487 °C:[17]

$$C_4H_2O_3 \rightarrow CO + CO_2 + C_2H_2.$$
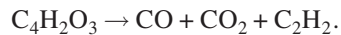
The highly reactive products allowed the fact that O can easily react with Mg to form MgO and C can easily substitute into the lattice of MgB_2. In order to qualitatively estimate the content of MgO, the relative intensity of the MgO (220) peak against the MgB_2 (110) peak are summarized in the inset of Fig. 1 for the three samples. Obviously, the relative intensity of the MgO peaks increases monotonically with increasing the oxygen content of dopants. If MgO is present between MgB_2 grains as insulating precipitates, it will have the effect of reducing the effective cross-sectional area of the sample, thereby blocking supercurrents. In addition, the position of both (100) and (110) peaks of doped samples shifts to higher angles, indicating a decrease of the a-axis lattice parameter. The shrinkage of a is attributed to the substitution of C for B.[6,18]

Figure 2 shows the typical SEM images of the fractured core layers for $C_4H_4O_4$ and $C_4H_2O_3$ doped tapes sintered at 800 °C, respectively. It can be seen that the $C_4H_2O_3$ doped

MgB_2 has a very dense structure with few voids compared to the $C_4H_4O_4$ doped sample, suggesting a good grain connectivity. From the higher magnification images, we cannot find observable difference in the MgB_2 grain size between two doped samples.

Figure 3 shows the transport J_c at 4.2 K in magnetic fields for the pure, $C_4H_2O_3$ and $C_4H_4O_4$ doped tapes. As can be seen from Fig. 3, both doped samples show a drastic enhancement of J_c compared with pure MgB_2 tapes. For instance, the level of enhancement in high magnetic fields for the tapes with $C_4H_2O_3$ is very similar to the level of J_c increase exhibited by nanoscale C doping.[7] In particular, the field dependence of J_c was also improved greatly, suggesting that H_{c2} was enhanced by the incorporation of C atoms into the MgB_2 crystal lattice. When we compare the $C_4H_2O_3$ and the $C_4H_4O_4$ doped tapes, we should note the difference of the J_c-B property. For the samples sintered at 800 °C, the J_c value of $C_4H_2O_3$ doped tape is about 2.6 times larger than that of $C_4H_4O_4$ doped tape in all measured magnetic fields, suggesting that the effective cross-sectional area of $C_4H_2O_3$ doped sample is higher than that of the $C_4H_4O_4$ doped one. The samples sintered at 850 °C show a similar behavior, although the J_c values of $C_4H_4O_4$ doped tapes are slightly higher than that of $C_4H_4O_4$-added samples heated at 800 °C. As were demonstrated by several authors,[14,19,20] intergranular MgO is an important current barrier in MgB_2 and it would cause a strong depression of transport J_c. Large amount of
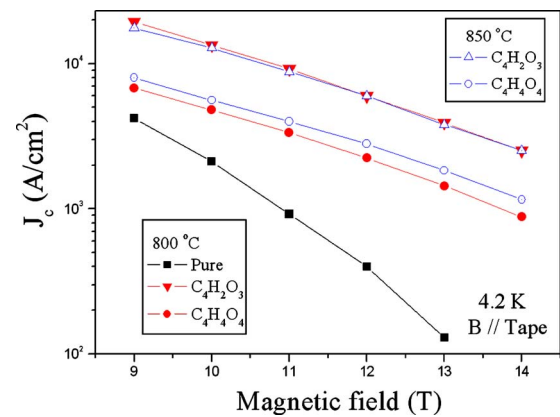

FIG. 2. SEM images of the $C_4H_2O_3$ doped [(a) and (c)] and $C_4H_4O_4$ doped [(b) and (d)] samples sintered at 800 °C after peeling off the Fe sheath.
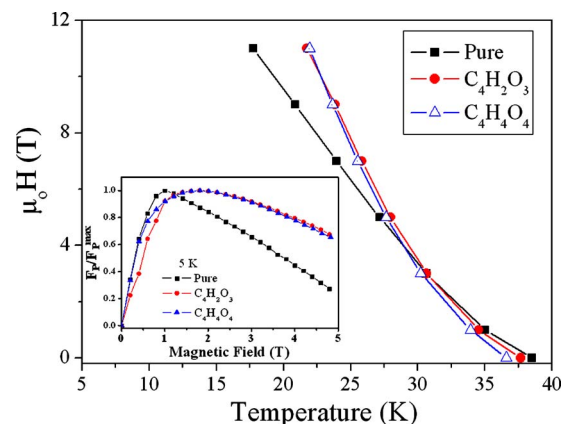

FIG. 4. (Color online) Temperature dependence of H_{c2} for the pure and doped tapes sintered at 800 °C. The inset shows the normalized volume pinning force F_P/F_P^{max} as a function of magnetic field at 5 K for the pure and doped tapes sintered at 800 °C.

TABLE I. Properties of the MgB$_2$ samples sintered at 800 °C as a function of dopants.

Sample	T_c (K)	$\rho_{300\,K}$ ($\mu\Omega$ cm)	$\rho_{40\,K}$ ($\mu\Omega$ cm)	RRR	A_F (%)	J_c (4.2 K, 10 T) ($\times 10^3$ A/cm^2)	H_{c2}(25 K) (T)
Pure	37.9	59.0	27.4	2.15	23.1	2.1	6.3
C$_4$H$_2$O$_3$	34.1	264.6	189.3	1.40	9.7	13.4	7.8
C$_4$H$_4$O$_4$	31.4	900.4	686.2	1.31	3.4	4.8	7.6

MgO as well as voids observed by XRD and SEM would create harmful weak links between the MgB$_2$ grains, hence, the J_c was greatly reduced in C$_4$H$_4$O$_4$ doped sample.

Figure 4 shows the temperature dependence of H_{c2} for the pure and doped tapes sintered at 800 °C. As we can see, the H_{c2} properties of the doped MgB$_2$ samples are significantly enhanced by C substitution into B sites. It is noted that the H_{c2} difference between two doped tapes at low temperature range are quite small, as shown in Fig. 4. This indicates that the impurity scattering of two doped tapes are on the same level.

The normalized volume pinning force F_P/F_P^{max} as a function of magnetic field at 5 K for the pure and doped tapes sintered at 800 °C is plotted in the inset of Fig. 4. It is clear that the pinning force of both doped samples show larger vortex pinning strength at higher magnetic fields than the pure samples. It is worthy to note that the transport J_c value of C$_4$H$_2$O$_3$ doped tapes was higher than that of C$_4$H$_4$O$_4$ doped tape, however, the normalized volume pinning force had almost no difference from each other at higher magnetic fields. This result indicates that the local, vortex pinning J_c of C$_4$H$_4$O$_4$ doped tape is as high as that of C$_4$H$_2$O$_3$ doped one, although its transport J_c was decreased by depression of connectivity.

Table I illustrates the measured ρ values, residual resistivity ratios (RRR $\rho_{300\,K}/\rho_{40\,K}$), active cross-sectional area fraction (A_F), J_c (10 T, 4.2 K), and H_{c2} (25 K) for the three kinds of MgB$_2$ tapes. To measure the ρ, the Fe sheath of the MgB$_2$ tape was removed. According to Rowell's analysis,[21] we estimate the A_F from the relation $A_F = \rho_{ideal}/[\rho_{300\,K} - \rho_{40\,K}]$, where $\rho(T)$ is our experimentally measured resistivity at temperature T and $\rho_{ideal} = 7.3$ $\mu\Omega$ cm.[22] The highest connection factor ($A_F = 23.1\%$) is observed in the pure tape. As can be seen, all doping greatly decreases the A_F values. $A_F = 9.7\%$ is seen for C$_4$H$_2$O$_3$ doped sample, while C$_4$H$_4$O$_4$ doped sample is only 3.4% connected. The small A_F values may be explained by the MgO present in the samples and by the samples' porosity. There are more MgO and porosity in C$_4$H$_4$O$_4$ doped samples, which are consistent with its lowest connectivity. On the other hand, the H$_2$O was formed by decomposition of C$_4$H$_4$O$_4$ would react with Mg or MgB$_2$, degrading the grain connectivity and grain linkages.[23]

The improvement of J_c-B performance in C$_4$H$_4$O$_4$ and C$_4$H$_2$O$_3$ doped samples can be attributed to a high density of flux pinning centers and increase of H_{c2} by C substitution for boron, as reported previously.[13] The two doped samples have similar flux pinning and H_{c2}, however, the transport J_c values are quite different from each other. From the XRD, SEM, and resistivity results, we can see that MgO or voids might be responsible for the low J_c values of C$_4$H$_4$O$_4$ doped tape. It should be pointed out that if the low transport J_c seen in C$_4$H$_4$O$_4$ doped sample is a result of lack of connectivity, then the J_c should be decreased by the same reduction in effective area. It is consistent with this speculation that the transport J_c decreases from 1.34×10^4 to 4.8×10^3 A/cm^2 at 10 T as the A_F value decreases from 9.7% to 3.4% for C$_4$H$_2$O$_3$ and C$_4$H$_4$O$_4$ doped samples heated at 800 °C.

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