Benzoic acid doping to enhance electromagnetic properties of MgB2 superconductors

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Abstract—The effect of benzoic acid doping on lattice parameters, microstructure, critical temperature ($T_C$), critical current density ($J_C$) and flux pinning force of MgB$_2$ has been studied. In this work we used benzoic acid as an example of aromatic acids as an additive to MgB$_2$. For different sintering process, actual carbon (C) substitution for boron (B) was estimated to be from 3.5 at% to 5.0 at% of B while $T_C$ dropped about 2–4 K. The advantages of aromatic acid doping include homogeneous mixing of precursor powders, avoidance of expansive nano-additives, production of highly reactive C and significant enhancement in $J_C$ of MgB$_2$, compared to undoped samples. High level C substitution of B can induce the MgB$_2$ crystals grow into bar shape microstructure. The $J_C$ value of 1.5 × 10$^5$ A cm$^{-2}$ at 5 K and 8 T for pre-heated 10 wt% C$_7$H$_6$O$_2$ doped MgB$_2$ sample is higher than that of the undoped MgB$_2$ by a factor of 13. As there are numerous aromatic acids readily available this finding has significant ramifications not only for the fabrication of MgB$_2$ but also for many C based compounds and composites.

Index Terms—Aromatic acids, benzoic acid, MgB$_2$, superconductivity.

I. INTRODUCTION

For the relatively high critical temperature ($T_C$) of about 39 K [1], the high critical current density ($J_C$) of more than 10$^5$ A cm$^{-2}$ in moderate fields, and the lack of weak links, magnesium diboride (MgB$_2$) superconductors is believed to be a promising candidate for engineering applications. The temperature range of choice is from 20 K to 30 K, for which the traditional low temperature superconductors (LTS) cannot play any role but a cryogen-free cooling system is readily available. Many works are devoted to the enhancement of the critical current density in applied magnetic field, invoking techniques like the chemical doping [2]–[14], irradiation [15], and various thermomechanical processing techniques [16]–[19]. Since MgB$_2$ has a relatively large coherence length and small anisotropy, the fluxoids to be pinned are string-like and amenable to pinning by inclusions and precipitates in the grains. This opens a window to the success of chemical doping in this material as chemical doping is a simple and readily scalable technique.

Various forms of carbon (C) dopants have remarkably enhanced the electromagnetic properties of MgB$_2$ [2]–[13]. Many novel techniques have been directed towards the fabrication of technically usable high-$J_C$ MgB$_2$ wires [2], [8], [10], [11]. Among the numerous forms of C-containing dopants, SiC doping has achieved a record high in-field $J_C$(B), $H_{c2}$, and irreversibility ($H_{irr}$) in MgB$_2$ [2], [9], [14]. These record properties have been confirmed and reproduced by other groups [8]–[11]. However, the best high field $J_C$ values achieved in the SiC doped MgB$_2$ wires were compromised by the reduction in self-field and low-field $J_C$. Although nanosize precursor particles were chosen for the doping process, it is difficult to achieve homogenous distribution of a small amount of nano-dopants within the matrix materials through solid state mixing. There are always agglomerates of nano-additives in the precursors. For various forms of C doping, the substitution of C for boron (B) can not be achieved at the same temperatures as that of the MgB$_2$ formation reaction due to their poor reactivity. Hydrocarbons, such as benzene, have been used for C substitution [20]. However, the C substitution level is limited by the high volatility of these compounds. In order to overcome these problems, some certain carbohydrates are proposed to be used as the dopants [21]. In this study, benzoic acid (C$_7$H$_6$O$_2$) is used as a representative of aromatic acid dopant. The lattice parameters (a and c), critical temperature ($T_C$), critical current density ($J_C$), flux pinning force ($F_p$), and microstructures are presented in comparison with that of the undoped reference MgB$_2$.

II. EXPERIMENTAL

MgB$_2$ superconductor bulks were prepared by an in-situ reaction process with the addition of benzoic acid (C$_7$H$_6$O$_2$). The selected amount of C$_7$H$_6$O$_2$ (99%), 10 wt% of total MgB$_2$, was dissolved in toluene (C$_7$H$_8$, 99.5%). The solution was mixed with an appropriate amount of amorphous B powder (99%, Tangshan, China). This slurry was dried in vacuum so that the B powder particles were coated by the C$_7$H$_6$O$_2$. Some of this uniform composite was then mixed with an appropriate amount of Mg (99%) powder. The other composite was pre-heated at 380°C in argon gas for 30 min to decompose the C$_7$H$_6$O$_2$ into benzene (C$_6$H$_6$) and carbon dioxide (CO$_2$), and then mixed with an appropriate amount of Mg (99%) powder. These mixed powders were ground in glove box, and pressed in closed tubes, and then sintered at 900°C for 30 min under high purity argon gas. The heating rate was 5°C/min.

All samples were characterized by X-ray diffraction (XRD) and field emission gun scanning electron microscopy (FEG-SEM). The crystal structure was refined with the aid of the program FullProf. $T_C$ was defined as the onset temperature at which diamagnetic properties were observed. The magnetization was...
measured at 5 K and 20 K using a Physical Property Measurement System (PPMS, Quantum Design) in a time-varying magnetic field with sweep rate 50 Oe/s and amplitude 8.5 T. Since there is a large sample size effect on the magnetic Jc for MgB2 [22], [23], all the samples for superconductivities measurement were made to the same size (1.0 mm × 2.2 mm × 3.5 mm) for comparison. The magnetic Jc was derived from the width of the magnetization loop using Bean’s model. Jc versus magnetic field was measured up to 8.5 T.

### III. RESULTS AND DISCUSSION

Table I shows the measured data for the undoped MgB2 and C7H6O2 doped MgB2 samples with different sintering processes. The lattice parameters calculated from XRD (shown in Fig. 1) show a large decrease in the a-axis parameter with 10 wt% C7H6O2 inclusions, especially in the preheated sample, but slight change in the c-axis parameter. This is an indication of the C substitution for B in the MgB2 lattices. The actual C substitution level can be estimated from the a-axis change [24]. It should be noted that the net C percentage addition is 68.84 wt% of the C7H6O2 addition. The actual C substitution levels of 3.5 at% to 5.0 at% of B at different processes are clearly higher than those with other forms of C dopants, which is attributable to the high reactivity of fresh C released from the decomposition of C7H6O2 at low temperature. For the preheating, C7H6O2 can decompose into C6H6 and CO2, more C atoms substitute for B in the closed sintering space. Accordingly, Tc of preheated sample decreases about 4 K than the undoped MgB2 for the intrinsic superconductivity has been damaged due to the C substitution. Table I also lists results of the AC susceptibility measurements as function of the temperature. With the increasing of C substitution from 3.5 at% to 5.0 at%, Tc decreases from 35.5 K to 33.5 K.

Fig. 2 shows the magnetic field dependence of Jc in all samples at 5 K and 20 K. The high-field Jc of the C7H6O2 doped MgB2 samples were much higher than that of the undoped MgB2. It should be noted that Jc values in high field were increased by more than an order of magnitude. For example, the Jc value of 1.5 × 10^4 A/cm^2 at 5 K and 8 T for preheated 10 wt% C7H6O2 doped MgB2 sample is higher than that of the undoped MgB2 by a factor of 13. Even though at 20 K and 5 T, the Jc value of preheated 10 wt% C7H6O2 doped MgB2 sample is higher than that of the undoped MgB2 by a factor of 6.5. In addition, there was no Jc degradation in self-field for the preheated 10 wt% C7H6O2 doped MgB2 sample. Moreover, Jc of preheated sample is slightly higher than that of the non-preheated one in the same applied measurement magnetic field. These findings can be further supported by the flux pinning results. Fig. 3 plots the field dependence of the volume pinning force, Fp = J × B, of all samples at 20 K. The Fp is normalized by the maximum volume pinning force, Fp,max. The flux pinning for the C7H6O2 doped MgB2 samples was significantly higher than that of the undoped one at B > 2.5 T. This result indicates that the Fp(B) of C7H6O2 doped MgB2 samples was improved by the C substitution effect and nano-C inclusions within the grains. The reaction producing free carbon is more effective than the other kinds of mechanically mixed carbon dopants.

Fig. 4 shows the SEM images for (a) undoped MgB2, (b) 10 wt% C7H6O2 doped MgB2, and (c) preheated 10 wt% C7H6O2 doped MgB2. The microstructure of undoped MgB2 sample appears inhomogeneous, consisting of crystalline grains from several tens of nm in size to 500 nm [Fig. 4(a)]. Although...
Fig. 3. Field dependence of the volume pinning force, $F_p = J \times B$, of undoped MgB$_2$ and 10 wt% benzoic acid doped MgB$_2$ at 20 K. The $F_p$ is normalized by the maximum volume pinning force, $F_{p,max}$.

grains are mixture of plates and bars, the morphology of the 10 wt% C$_7$H$_6$O$_2$ doped MgB$_2$ sample was refined to smaller, denser, and more homogeneous grains compared to the undoped MgB$_2$ one. As to the preheated sample, however, grains appear to have a bars and larger plates shape, with their width up to 250 nm and length up to 600 nm, in a well connected grain network [Fig. 4(c)]. The SEM images suggest that the higher C substitution level induces the MgB$_2$ growing into a bar-shape grains microstructure to remedy the distortion of lattices. Although the distorted lattices result in the $T_c$ decrease, they can afford many defects in the superconductor as strong flux pinning centers to drag the flux movement. The grain refinement effect by 10 wt% C$_7$H$_6$O$_2$ doping is supported by the FWHM results derived from XRD patterns. The small MgB$_2$ grains are effective in enhancing flux pinning because the grain boundaries of MgB$_2$ act as the effective pinning centers, as in the case of A15 metallic superconductors. The fine microstructures improve the crystals’ linkage enhancing effective current path.

Using organic solution, such as toluene, to dissolve the aromatic acid, such as benzoic acid, for manufacturing MgB$_2$ superconductors shows significant advantages in the raw materials mixing process. Aromatic acids can be dissolved in a suited volatilizable solvent so that the solution can form slurry with B powder. After evaporating the solvent the aromatic acid forms a coating on the B powder surfaces, giving a highly uniform mixture. The aromatic acids in the mixture melt at lower temperatures and decompose at temperatures below the formation temperature of MgB$_2$, hence producing highly reactive and fresh C on the atomic scale, which can substitute B easily than the other kinds of C. For the freshly formed C elements are high reactivity, the C substitution for B can take place at the same temperature as the formation temperature of MgB$_2$. The simultaneous dual reactions promote C substitution for B in the lattice and the inclusion of excess C within the grains, resulting in the enhancement of $J_c$, and inevitably, in the depression of $T_c$.

Fig. 4. The microstructure photographs from field emission gun-scanning electron microscopy (FEG-SEM): (a) undoped MgB$_2$, (b) 10 wt% C$_7$H$_6$O$_2$ doped MgB$_2$, and (c) preheated 10 wt% C$_7$H$_6$O$_2$ doped MgB$_2$.

IV. CONCLUSION

In summary, benzoic acid doping results in a depression in $T_c$ but significantly increases the C substitution level, reduces the agglomerate impurities, and hence improves $J_c$ performance at all the operating temperatures and especially in the high field range. Manufacturing nano-doped materials using the organic solution route solves the agglomeration problem, avoids the use of expensive nano-additives, and achieves improved performance properties for aromatic acids are soluble, cheap, abundant, and readily available. As aromatic acids consist of a large range of materials, this work will have significant implications for further improvement of the performance properties of MgB$_2$, as well as many other C-based compounds and composites.
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