Strong enhancement of critical current density in MgB$_2$ superconductor using carbohydrate doping

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With the relatively high critical temperature ($T_c$) of 39 K$^1$ and the high critical current density ($J_c$) of $> 10^5$ Acm$^{-2}$ in moderate fields, magnesium diboride (MgB$_2$) superconductors could offer the promise of important large-scale and electronic device applications to be operated at 20 K. A significant enhancement in the electromagnetic properties of MgB$_2$ has been achieved through doping with various form of carbon (C)$^2$-$^{13}$. However, doping effect has been limited by the agglomeration of nano-sized dopants and the poor reactivity of C containing dopants with MgB$_2$. Un-reacted dopants result in a reduction of superconductor volume. In this work, we demonstrate the advantages of carbohydrate doping over other dopants, resulting in an increase of in-field $J_c$ by more than one order of magnitude without any degradation of self-field $J_c$. As there are numerous carbohydrates readily available this finding has significant ramifications not only for the fabrication of MgB$_2$ but also for many C based compounds and composites.

Many of the important applications of superconductors require the maintenance of high $J_c$ in strong magnetic fields. MgB$_2$ has been fabricated in various forms: single crystals, bulk, thin films, tapes and wires. Various novel techniques have been directed towards the fabrication of technically usable high-$J_c$ MgB$_2$ wires$^2$,$^8$,$^{10}$,$^{11}$. The performance of MgB$_2$ can rival and exceed that of conventional superconductors. To take advantage of its $T_c$ of 39K, enhancements of the both upper critical field ($H_c^2$) and $J_c$ are essential. Attempts to accomplish this have invoked the introduction of numerous techniques including chemical doping$^2$-$^{14}$, irradiation$^15$, and various thermo-mechanical processing techniques$^{16}$-$^{19}$. Chemical doping is a simple and readily scalable technique. 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.

Among the numerous forms of C-containing dopants, SiC doping has achieved a record high in-field $J_c(B)$, $H_c^2$, and irreversibility ($H_{irr}$) in MgB$_2$$^2$,$^9$,$^{14}$. These record high properties have been confirmed and reproduced by many groups$^8$-$^{11}$, and the performance records remain unbroken up to now. 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 a great challenge 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 we proposed to use a carbohydrate such as DL-malic acid (C$_4$H$_6$O$_5$) as the dopant. The significant advantages of carbohydrate doping are: (1) Carbohydrates can be dissolved in a solvent so that the solution can form a slurry with B powder. After evaporating the solvent the carbohydrate forms a coating on the B powder surfaces, giving a highly uniform mixture. (2) The carbohydrates 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, as well as a reducing reagent, carbon monoxide, which may convert boron oxide to B, reducing the impurities in B powder. (3) Because of the high reactivity of the freshly formed C, 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 $J_c$, $H_{irr}$, and $H_{c2}$.

In this study, we used malic acid as a representative of carbohydrate dopant. We fabricated MgB$_2$ superconductor with malic acid doping included. The lattice parameters, critical temperature ($T_c$), $J_c$, $H_{irr}$, $H_{c2}$, and microstructures are presented in comparison with the un-doped reference MgB$_2$. MgB$_2$ pellets were prepared by an in-situ reaction process with the addition of malic acid, C$_4$H$_6$O$_5$. The selected amount of C$_4$H$_6$O$_5$ (99%), from 0 to 30wt% of total MgB$_2$, was dissolved in toluene (C$_7$H$_8$, 99.5%). The solution was mixed with an appropriate amount of B (99%) powder. This slurry was dried in vacuum so that the B powder particles were coated by the C$_4$H$_6$O$_5$. This uniform composite was then mixed with an appropriate amount of Mg (99%) powder. These mixed powders were ground, pressed, 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. In addition, $H_{c2}$ and $H_{irr}$ were defined as $H_{c2}=0.9R(T_c)$ and $H_{irr}=0.1R(T_c)$ from the resistance ($R$) versus temperature ($T$) curve. The magnetization was measured at 5 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 $J_c$ for MgB$_2$$^{22,23}$ all the samples for measurement were made to the same size (1 x 2.2 x 3.3 mm$^3$) for comparison. The magnetic $J_c$ was derived from the width of the magnetization loop using Bean’s model. $J_c$ versus magnetic field was measured up to 8.5 T.
Table 1 shows the measured data for the un-doped MgB$_2$ and MgB$_2$+C$_4$H$_6$O$_5$ samples with different addition levels. The lattice parameters calculated from XRD show a large decrease in the $a$-axis parameter with 10wt% C$_4$H$_6$O$_5$ and a small further drop in $a$ with increasing C$_4$H$_6$O$_5$ addition level, but no change in the $c$-axis parameter. This is an indication of the C substitution for B. The actual C substitution level can be estimated from the $a$-axis change$^{21}$. It should be noted that the net C percentage addition is only 36% of the C$_4$H$_6$O$_5$ addition. The actual C substitution levels of 1.9at% to 2.3at% of B at three doping levels 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 C$_4$H$_6$O$_5$ at low temperature (~150°C). The increase in sintering temperature improves both the crystallinity and the C substitution for B. The former will increase $T_c$, while the latter will decrease $T_c$. As a compromise, these two opposing factors result in a high level of C substitution for B with a relatively small drop in $T_c$. The high-field $J_c$s of the MgB$_2$+C$_4$H$_6$O$_5$ samples were much higher than that of the un-doped MgB$_2$. Specifically, it should be noted that the self-field $J_c$ of MgB$_2$+C$_4$H$_6$O$_5$ samples was not reduced at doping levels as high as 30wt% C$_4$H$_6$O$_5$, hence the connectivity between MgB$_2$ grains was not affected by doping with C$_4$H$_6$O$_5$. Although there is a possibility of the formation of H$_2$O during sintering due to the decomposition of C$_4$H$_6$O$_5$, there was no degradation in self-field $J_c$, even for 30wt% C$_4$H$_6$O$_5$ added to MgB$_2$. This may be attributable to the fact that the decomposition products, C and CO, of C$_4$H$_6$O$_5$ reduced B$_2$O$_3$ and hence increased the effective cross section of the superconductor.

Figure 1(a) shows the magnetic field dependence of $J_c$ in all samples at 20 K and 5 K. It should be noted that $J_c$ values in high field were increased by more than an order of magnitude. For example, the $J_c$ value of 2.5 x 10$^9$ Acm$^{-2}$ at 5 K and 8 T for MgB$_2$+30wt% C$_4$H$_6$O$_5$ sample is higher than that of the un-doped MgB$_2$ by a factor of 21. In addition, there was no $J_c$ degradation in self-field for the MgB$_2$+30wt% C$_4$H$_6$O$_5$ sample. These findings can be further supported by the flux pinning results. Fig 1(b) plots the field dependence of the volume pinning force, $F_p$=$J_c$ x $B$, of all samples at 20 K. The $F_p$ is normalized by the maximum volume pinning force, $F_{p,max}$. The flux pinning for the MgB$_2$+C$_4$H$_6$O$_5$ samples was significantly higher than that of the un-doped one at $B$>1.5 T. This result indicates that the $F_p(B)$ of MgB$_2$+C$_4$H$_6$O$_5$ samples was improved by the C substitution effect and nano-C inclusions within the grains.

The normalized temperature dependence of $H_{irr}$ and $H_{c2}$ for all samples is shown in Figure 2. Significantly enhanced $H_{irr}$ and $H_{c2}$ for MgB$_2$+C$_4$H$_6$O$_5$ samples were observed, suggesting that C substitution into B sites results in an enhancement in $H_{irr}$ and $H_{c2}$. The steeper slopes of $H_{irr}$ for MgB$_2$+C$_4$H$_6$O$_5$ samples exceeded $H_{c2}$ of un-doped MgB$_2$ below a temperature of 22 K. The resistivity, $\rho$, for the un-doped and MgB$_2$+C$_4$H$_6$O$_5$ samples is 34 and 80-90 $\mu$Ω·cm at 40 K, respectively, as shown in Table 1. The increased resistivity for MgB$_2$+C$_4$H$_6$O$_5$ samples indicates the increased impurity scattering as a result of C substitution into B sites.
FEG-SEM images for (a) un-doped MgB$_2$, (b) MgB$_2$+10wt% C$_4$H$_6$O$_5$, and (c) MgB$_2$+30wt% C$_4$H$_6$O$_5$ are shown in Figure 3. The un-doped MgB$_2$ sample appears inhomogeneous, consisting of crystalline grains from several tens of nm in size to 500nm. The morphology of the MgB$_2$+10wt% C$_4$H$_6$O$_5$ sample was refined to smaller, denser, and more homogeneous grains compared to the un-doped MgB$_2$ one. The grain refinement by 10 wt% and 20 wt% C$_4$H$_6$O$_5$ doping is supported by the FWHM results for all the peaks as shown in Fig. 4. The small MgB$_2$ grains are effective in enhancing flux pinning because the grain boundaries of MgB$_2$ act as effective pinning centers, as in the case of A15 metallic superconductors. As the doping level further increases to 30wt%, however, grains appear to have a bar/plate shape, with their width up to 150 nm and length up to 400 nm, in a well connected grain network (Figure 3(c)). Consistent with the FEG-SEM image is the decrease in FWHM for the 30 wt% doped sample (Figure 4) although the average FWHM values for all peaks are still bigger than those of the un-doped sample. The FEG-SEM image suggests that at higher doping levels C$_4$H$_6$O$_5$ may act as a sintering aid to improve the crystallinity. The grain growth should not improve the electromagnetic properties. However, this effect may be offset by the increase in C substitution level, the reduction in resistivity (Table 1), and improvement in grain connectivity. This is well evidenced by the fact that the self-field $J_c$ of the MgB$_2$+30wt% C$_4$H$_6$O$_5$ sample was enhanced while the improved in-field $J_c$, $H_{irr}$, and $H_{c2}$ were maintained, as shown in Figures 1 and 2.

In summary, carbohydrate doping results in a small depression in $T_c$ but significantly increases the C substitution level, reduces the impurities, and hence improves $J_c$, $H_{irr}$, and $H_{c2}$ performance at all the operating temperatures and over the entire field range. Carbohydrates are cheap, abundant, and readily available. This finding opens a new direction for the manufacture of nano-doped materials using the carbohydrate solution route, which solves the agglomeration problem, avoids the use of expensive nano-additives, and achieves improved performance properties. As carbohydrates 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.

**Acknowledgements**

The authors gratefully acknowledge financial support from the Australian Research Council, Hyper Tech Research Inc, and CMS Alphatech International Ltd.

The authors declare no conflict financial interest in this work.

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Figure captions

Table 1. Measured data for un-doped MgB$_2$ and MgB$_2$+C$_4$H$_6$O$_5$ samples with different addition levels.

Figure 1. Superconducting properties of un-doped MgB$_2$ and MgB$_2$+C$_4$H$_6$O$_5$ samples with different addition levels: (a) Magnetic field dependence of $J_c$ in all samples at 20 K and 5 K; (b) Field dependence of the volume pinning force, $F_p=J \times B$, of all samples at 20 K. The $F_p$ is normalized by the maximum volume pinning force, $F_{p,max}$.

Figure 2. Normalized temperature dependence of $H_{irr}$ and $H_{c2}$ for un-doped and C$_4$H$_6$O$_5$ doped samples. $H_{c2}$ and $H_{irr}$ were defined as $H_{c2}=0.9R(T_c)$ and $H_{irr}=0.1R(T_c)$ from the $R$ versus $T$ curve.

Figure 3. The photographs from field emission gun-scanning electron microscopy (FEG-SEM): (a) Un-doped MgB$_2$; (b) MgB$_2$+10wt% C$_4$H$_6$O$_5$; (c) MgB$_2$+30wt% C$_4$H$_6$O$_5$.

Figure 4. Full width at half maximum (FWHM) as a function of amount of C$_4$H$_6$O$_5$. MgB$_2$ (100), (101), (002), and (110) correspond to $2\theta \sim 33.6^\circ$, 42.5$^\circ$, 52.0$^\circ$, and 60.0$^\circ$, respectively.
Table 1.

| DL-malic acid amount (wt%) | Lattice parameters | Actual C (x) in MgB$_{2-x}$C$_{x}$ † | $T_c$ (K) | $\rho_{40 K}$ (\(\mu\Omega\cdot cm\)) | $\rho_{300 K}$ (\(\mu\Omega\cdot cm\)) | $H_{irr}^*$ (T) (20 K) | Self-field (20 K) | $J_c$ (Acm$^{-2}$) | $8 \, T$ (5 K) |
|---------------------------|------------------|-----------------------------------|----------|---------------------------------|---------------------------------|-------------------|-----------------|---------------|---------------|
| 0                         | 3.08355          | 3.52175                           | 37.6     | 34.5                            | 73.5                            | 5.4               | 3.9 x 10⁷       | 0.1 x 10⁴     |
| 10 (3.6 wt% C)            | 3.07516          | 3.52683                           | 0.0380   | 35.8                            | 90.2                            | 6.7               | 3.5 x 10⁷       | 2.3 x 10⁴     |
| 20 (7.2 wt% C)            | 3.07464          | 3.52297                           | 0.0404   | 35.7                            | 83.8                            | 6.8               | 3.5 x 10⁷       | 2.7 x 10⁴     |
| 30 (10.8 wt% C)           | 3.07319          | 3.52147                           | 0.0460   | 35.8                            | 79.6                            | 6.7               | 4.0 x 10⁷       | 2.6 x 10⁴     |

† extrapolation from measured lattice parameters

$H_{irr}^*$ was calculated from the standard criterion of critical current density (100 Acm$^{-2}$)
Figure 1
Figure 2.
Figure 3.
Figure 4.